Supplementary Information

Organometallic Gold(III) Reagents for Cysteine Arylation

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I. General Information

Methods and Materials

Reagent Information:

All commercially available chemicals were used as received unless otherwise stated. The Au(THT)Cl and (RuPhos)Pd(tolyl)I complexes were prepared according to literature procedures.[1,2] Dry solvents were obtained from Grubbs columns with activated alumina and copper catalysts and stored in a Vacuum Atmospheres glovebox over 4Å molecular sieves. *O*-carborane was purchased from Boron Specialties (USA). Phosphorus trichloride (98%), *N,N'*-diisopropylethylenediamine (97%), chlorobis(3,5-dimethylphenyl)phosphine (90%), and silver bis(trifluoromethanesulfonyl)imide ($AgNTf_2$) were purchased from Alfa Aesar. *N,N'*-Di-*tert*-butylethylenediamine (98%), chloro[di(1-adamantyl)-2-dimethylaminophenylphosphine]gold(I), 2-iodonaphthalene (99%), 4-iodotoluene (99%), and L-glutathione reduced (BioXtra grade) were purchased from Sigma-Aldrich. Silver hexafluoroantimonate ($AgSbF_6$) (98%), silver tetrafluoroborate ($AgBF_4$) (98%), 4-iodobenzotrifluoride (98%), 1-fluoro-4-iodo-benzene (99%), 1-bromo-4-iodobenzene (99%), 4-iodophenol (98%), 2-iodopyridine (98%), 4-iodoaniline (98%) and 4-(trifluoromethoxy)iodobenzene (97%) were purchased from Oakwood Chemical. Trametinib (GSK1120212, 99%), and 1-ethyl-4-iodobenzene (98%) were purchased from Fisher Scientific. Monodisperse PEG_{12} was purchased form JenKem Technology USA. 1-Hydroxy-7-azabenzotriazole solution (HOAt, 0.6 M in DMF), 1-[Bis(dimethylamino)methylene]-1H-1,2,3-triazolo[4,5-b]pyridinium 3-oxid hexafluorophosphate (HATU), *N,N,N',N'*-Tetramethyl-*O*-(1*H*-benzotriazol-1-yl)uronium hexafluorophosphate (HBTU), D-Biotin, Fmoc-Rink amide linker, Fmoc-L-Arg(Pbf)-OH, Fmoc-L-Ala-OH, Fmoc-L-Cys(Trt)-OH, Fmoc-L-Gly-OH, Fmoc-L-Asp(OtBu)-OH, Fmoc-L-Ser(tBu)-OH, Fmoc-L-Lys(Boc)-OH were purchased from Chem-Impex International.

General Analytical Information:

NMR spectra were recorded on DRX 400, DRX 500, and AVIII 500 Bruker spectrometers at 400 or 500 MHz (^1H), 125 MHz (^{13}C), 282 MHz (^{19}F), 80 MHz (^{11}B), and 121 MHz (^{31}P). Spectra are reported in δ (parts per million) relative to residual protio-solvent signals for ^1H and ^{13}C, C_6H_5F -(δ -113.15 ppm) for ^{19}F, $BF_3{\cdot}Et_2O$ (δ 0.00 ppm) for ^{11}B, and H_3PO_4 (δ 0.00 ppm) for ^{31}P. Deuterated solvents (Cambridge Isotope Laboratories) used for NMR spectroscopic analyses were stored over 4Å molecular sieves. Electrospray ionization mass spectra of small molecules and Au-based complexes (ESI-MS(+)) were collected on a Waters LCT premier mass spectrometer. Samples were prepared in MeCN at concentrations <1 μM, and the data were processed using the program mMass Version 5.4.1.0.

Peptide Purification and LC-MS Analysis:

Peptide purification was carried out on an Agilent Technologies 1260 Infinity II HPLC system equipped with an Agilent ZORBAX 300SB-C18 column (5 μm, 9.4 × 250 mm) using 0.1% TFA in water and 0.1% TFA in acetonitrile as the eluent. Data were processed using Agilent Mass Hunter software. Deconvoluted mass spectra of proteins were gathered using maximum entropy setting. Peptide modification yield was calculated *s* integrations of the peptide and modified peptide peaks in the TIC spectra using the following formula: $(I_{[MP]}/I_{[MP+SP]})\times 100$ where $I_{[MP]}$ is the integration of the modified peptide peak and $I_{[MP+SP]}$ is the sum of integrations of the modified peptide peak and the starting peptide peak.

Peptide Purification Method Information: Column temperature: 23 °C. Flow rate: 3 mL/min. Gradient: 95-60% water (0.1% TFA) over 22 min.

LC-MS analysis was carried out using an Agilent 6530 ESI-Q-TOF. Peptide and DARPin analyses were carried out using an Agilent ZORBAX 300SB C18 column (5 µm, 2.1 × 500 mm). Analysis of FGF2 was carried out using an Agilent ZORBAX 300SB C3 column (3.5 µm, 3.0 × 150 mm) using 0.1% TFA in water and 0.1% TFA in acetonitrile as the eluent.

LC-MS Method Information:

Method used for peptides: Column temperature: 23 °C. Flow rate: 0.8 mL/min. Gradient: 99% water (0.1% formic acid (FA)) for 2 minutes; 99%-91% water (0.1% FA) 2-11 minutes; 5% water (0.1% FA) from 12-15 min.

Method used for proteins: Column temperature: 23 °C. Flow rate: 0.8 mL/min. Gradient: 99% water (0.1% formic acid (FA)) for 2 minutes; 99%-9% water (0.1% FA) 2-11 minutes; 5% water (0.1% FA) from 11-12 min.

MS/MS analysis was performed using a 30 eV collision energy and fragment analysis was carried out using ProSight Lite software.

ICP-AES Measurements

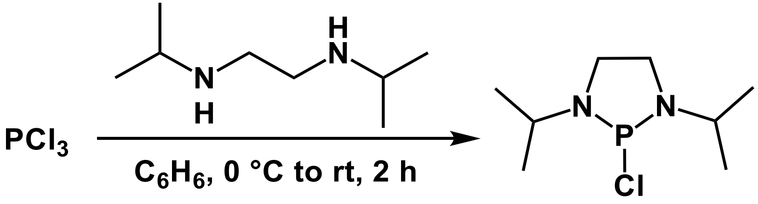
Gold ICP-AES analyses were conducted using a Shimadzu ICPE-9000 inductively coupled plasma atomic emission spectrometer (ICP-AES). Solutions of standard concentrations were used for calibration purposes and were prepared from a gold standard solution purchased from Sigma Aldrich, designated suitable for ICP analysis. Standard solutions were prepared with concentrations of 50, 100, 300, and 600 ppb in 2% OmniTrace HCl diluted with Milli-Q H_2O, and analyses were run at $\lambda = 242.795$ nm.

II. Synthetic Procedures

Purification of *o*-carborane purchased from Boron Specialties

A round bottom flask was charged with a solution of *o*-carborane (15 g, 10 mmol) in MeOH (150 mL). 12 M HCl (50 mL) was added slowly to the reaction vessel, and the resulting mixture was heated to 50 °C and stirred overnight. The solution was then cooled to room temperature, and H_2O (200 mL) was added, resulting in the precipitation of white solids that were isolated by vacuum filtration, washed with water, and air dried. The solid was then dissolved in CH_2Cl_2, dried over $MgSO_4$, and filtered through Celite. The filtrate was dried *in vacuo* to afford a white powder. The powder was then sublimed at 60 °C under dynamic vacuum. After sublimation away from the yellow residue, the white crystals were taken up in $C_2H_4Cl_2$, suspended with activated carbon/charcoal, and stirred for 2-3 hours at 75 °C. The suspension was then filtered through a pad of Celite, and the filtrate was evaporated under vacuum. The resulting white solid was again sublimed at 60 °C to produce white crystals.

Synthesis of 1,3-diisopropyl-2-chloro-1,3,2-diazaphospholidine



Phosphorus trichloride (483 µL, 5.55 mmol, 1.00 equiv) was added to C_6H_6 (7 mL), and the solution was cooled to 0 °C. Once at 0 °C, a solution of *N,N'*-diisopropylethylenediamine (1.0 mL, 5.6 mmol, 1.0 equiv) and triethylamine (787 µL, 5.55 mmol, 1.00 equiv) in C_6H_6 (8 mL) cooled to 0 °C, was added dropwise slowly to the solution containing phosphorus trichloride. White precipitate formed immediately upon addition. The suspension was then stirred at room temperature for 2 h. After 2 h, the precipitate was filtered off and the filtrate was concentrated under reduced pressure to afford the pure product as a yellow oil in quantitative yield.

The product is unstable in open atmosphere, and a degradation product was observed by ^{31}P NMR spectroscopy (δ ~7 ppm in CH_2Cl_2) within minutes of exposure to air. All manipulations with this product were conducted in a glovebox under an atmosphere of purified N_2 and with dried and degassed reagents and solvents.

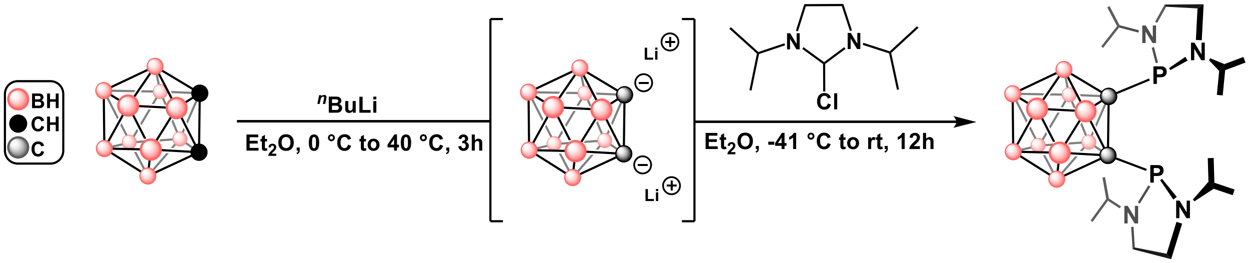
^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ 3.48-3.42 (m, 2H, C*H*), 3.32 (s, 2H, C*H*2), 3.31 (s, 2H, CH_2), 1.30 (d, 12H, CH_3, J = 6.6 Hz) ppm.

^{13}C{^{1}H} NMR (125 MHz, CD_2Cl_2, 298 K): δ 48.90 (*C*H), 47.25 (CH_2), 22.20 (CH_3) ppm.

^{31}P{^{1}H} NMR (121 MHz, CD_2Cl_2, 298 K): δ 168.0 ppm.

Synthesis of 1,2-bis(diaminophosphino)-1,2-dicarba-*closo*-dodecaborane

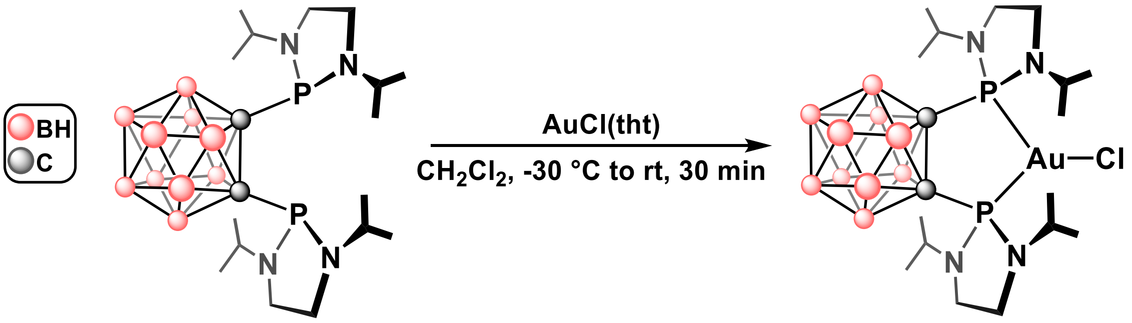
Syntheses and full characterization for 1,2-Bis(diaminophosphino)-1,2-dicarba-closo-dodecaborane compounds shown below can be found in the literature.[3] Adapted syntheses are included here for convenience.



A round bottom flask was charged with a solution of *o*-carborane (318 mg, 2.20 mmol, 1.00 equiv) in Et_2O (5 mL) under an atmosphere of N_2, and the temperature of the solution was lowered to 0 °C. Once at 0 °C, ^{n}BuLi (2.5 M in hexane, 1.85 mL, 4.63 mmol, 2.10 equiv) was added dropwise, resulting in the formation of white precipitate. After complete addition, the mixture was refluxed at 40 °C for 3 h. After 3 h, the reaction temperature was lowered to -41 °C, at which point a solution of 1,3-diisopropyl-2-chloro-1,3,2-diazaphospholidine (1.15 g, 2.20 mmol, 2.50 equiv) in Et_2O (12 mL) was added via cannula transfer. The formation of an off-white precipitate was observed upon complete addition, at which point the reaction was allowed to warm to room temperature, and then stirred for 12 h. After 12 h, complete consumption of the starting materials was confirmed by TLC, and the solvent was evaporated under reduced pressure to yield an off-white solid. This solid was subjected to flash chromatography in a hexane and acetone (95:5) mixture to yield the pure product as a white solid (Rf = 0.77). The product was further purified *via* crystallization in dichloromethane layered with *n*-pentane at -30 °C.
The product was isolated as a white and crystalline solid and is stable for months when stored in the solid state under an N_2 atmosphere at -30 °C.

^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$, 298 K): δ 112.6 ppm.

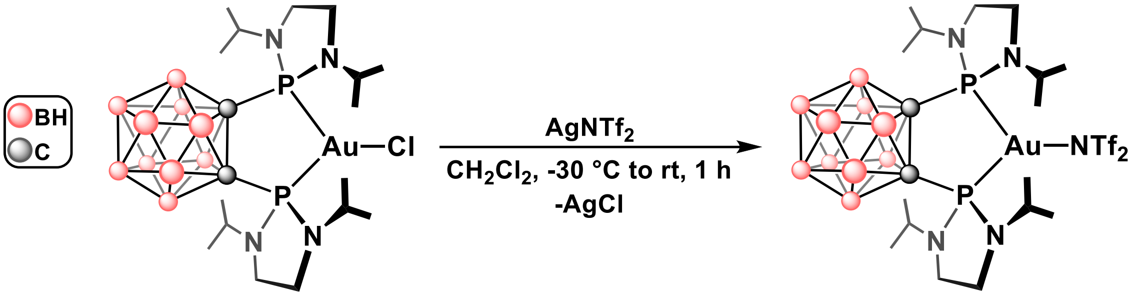
Synthesis of (DPCb)AuCl ((1,2-bis(1,3-diisopropyl-1,3,2-diazaphospholidin-2-yl)-1,2-dicarba-*closo*-dodecaborane)AuCl)



In the glovebox, a solution of 1,2-bis(1,3-diisopropyl-1,3,2-diazaphospholidin-2-yl)-1,2-dicarba-*closo*-dodecaborane (DPCb, 65 mg, 0.13 mmol, 1.0 equiv) in CH_2Cl_2 (4 mL) was cooled to -30 °C. This solution was then added dropwise to a cooled solution (-30 °C) of AuCl(tht) (43 mg, 0.13 mmol, 1.0 equiv) in CH_2Cl_2 (4 mL) over the course of 5 min. After stirring at room temperature for 30 min, the solution was concentrated *in vacuo* to afford the crude (DPCb)AuCl complex as a white solid. The crude material was purified *via* crystallization from a concentrated solution of CH_2Cl_2 layered with *n*-pentane at -30 °C. The pure product was isolated as a white crystalline solid that is yellow in solution, and the product is stable for months when stored in the solid state under an N_2 atmosphere at -30 °C.

$^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$, 298 K): δ 116.6 ppm.

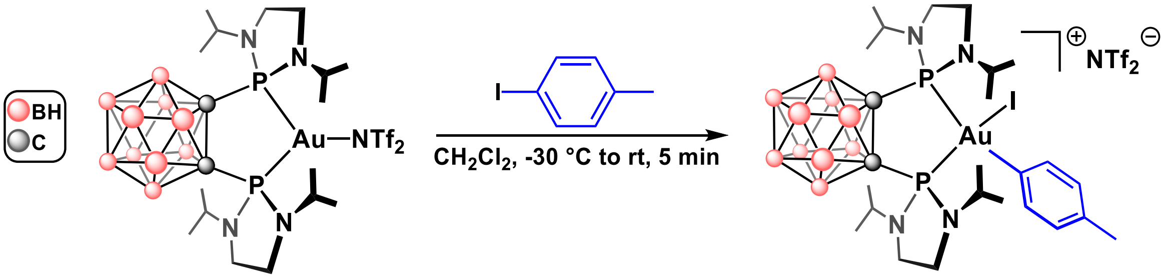
Synthesis of (DPCb)AuNTf



In the glovebox, a CH_2Cl_2 (7 mL) solution of (DPCb)AuCl (91 mg, 0.12 mmol, 1.0 equiv) was cooled to -30 °C. This solution was then added dropwise to a cooled suspension (-30 °C) of $AgNTf_2$ (49 mg, 0.12 mmol, 1.0 equiv) in CH_2Cl_2 (8 mL) over 5 min under protection from light. The reaction mixture was allowed to warm to room temperature, and after 1 h of stirring, the suspension was filtered through a pad of Celite and the filtrate was concentrated *in vacuo* to afford the (DPCb)$AuNTf_2$ product as a yellow solid. The product was used without further purification and is stable for months when stored in the solid state under an N_2 atmosphere at -30 °C.

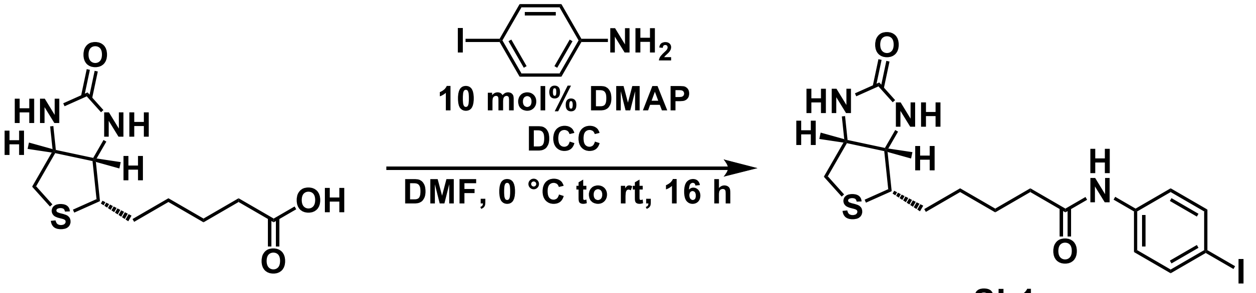
$^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$, 298 K): δ 138.3 ppm.

Synthesis of 1



In the glovebox, a solution of (DPCb)AuNTf$_2$ (10 mg, 0.010 mmol, 1.0 equiv) in CH$_2$Cl$_2$ (350 μL) was cooled to -30 °C. To this cold solution was added a cooled (-30 °C) solution of 4-iodotoluene (12 mg, 0.053 mmol, 5.0 equiv) in CH$_2$Cl$_2$ (350 μL). The reaction was allowed to warm to room temperature for 5 min, during which time a color change to dark yellow was observed. The yellow solution was concentrated *in vacuo* to afford the product as a yellow solid. The isolated material was used for bioconjugation studies without further purification.

^{31}P{^{1}H} NMR (121 MHz, CH$_2$Cl$_2$, 298 K): δ 132.09 (d, *J* = 22.7 Hz), 124.01 (d, *J* = 22.8 Hz) ppm.



SI-1

Aryl iodide substituted biotin (**SI-1**) was synthesized following Steglich esterification conditions.[4]

A 2-neck round bottom flask was charged with a solution biotin (217 mg, 0.890 mmol, 1.00 equiv) in dry DMF (5 mL) under an atmosphere of Ar. To this solution was added DMAP (11 mg, 0.080 mmol, 10 mol%) and 4-iodoaniline (778 mg, 3.55 mmol, 4.00 equiv) under stirring. The temperature of the reaction mixture was lowered to 0 ˚C, at which point a solution of DCC (202 mg, 0.980 mmol, 1.10 equiv) in DMF (5 mL) was added dropwise under stirring. The reaction mixture was allowed to warm to room temperature and then stirred for an additional 16 h. After 16 h, the solution was concentrated under reduced pressure, and CH_2Cl_2 (25 mL) was added, resulting in the precipitation of colorless solids that were isolated by filtration, washed with CH_2Cl_2 (2 × 25 mL) and then methanol (2 × 25 mL) to afford the product as a white solid.

^{1}H NMR (400 MHz, DMSO-*d*$_6$): δ 9.96 (s, 1H, -N*H*), 7.61 (d, 2H, *J* = 8.8 Hz, H_{Ar}), 7.43 (d, 2H, *J* = 8.8, H_{Ar}), 6.42 (s, 1H, -N*H*), 6.35 (s, 1H, -N*H*), 4.30 (m, 1H), 4.22–4.08 (m, 1H), 3.17–3.08 (m, 1H, $-CH_2SC\mathit{H}CH_2-$), 2.82 (dd, 1H, *J* = 12.4 Hz, 5.1 Hz, $-C\mathit{H}_2SCHCH_2-$), 2.57 (d, 1H, *J* = 12.4 Hz, $-C\mathit{H}_2SCHCH_2-$), 2.30 (t, 2H, *J* = 7.4 Hz, $-C\mathit{H}_2CONH-$), 1.70–1.53 (m, 2H, $-C\mathit{H}_2$), 1.55–1.48 (m, 2H, $-C\mathit{H}_2$), 1.36 (m, 2H, $-C\mathit{H}_2$) ppm.

^{13}C NMR (125 MHz, DMSO-*d*$_6$): δ 174.48, 171.36, 162.71, 139.13, 137.29, 121.23, 61.04, 59.20, 55.39, 36.26, 33.36, 28.22, 28.09, 25.02 ppm.

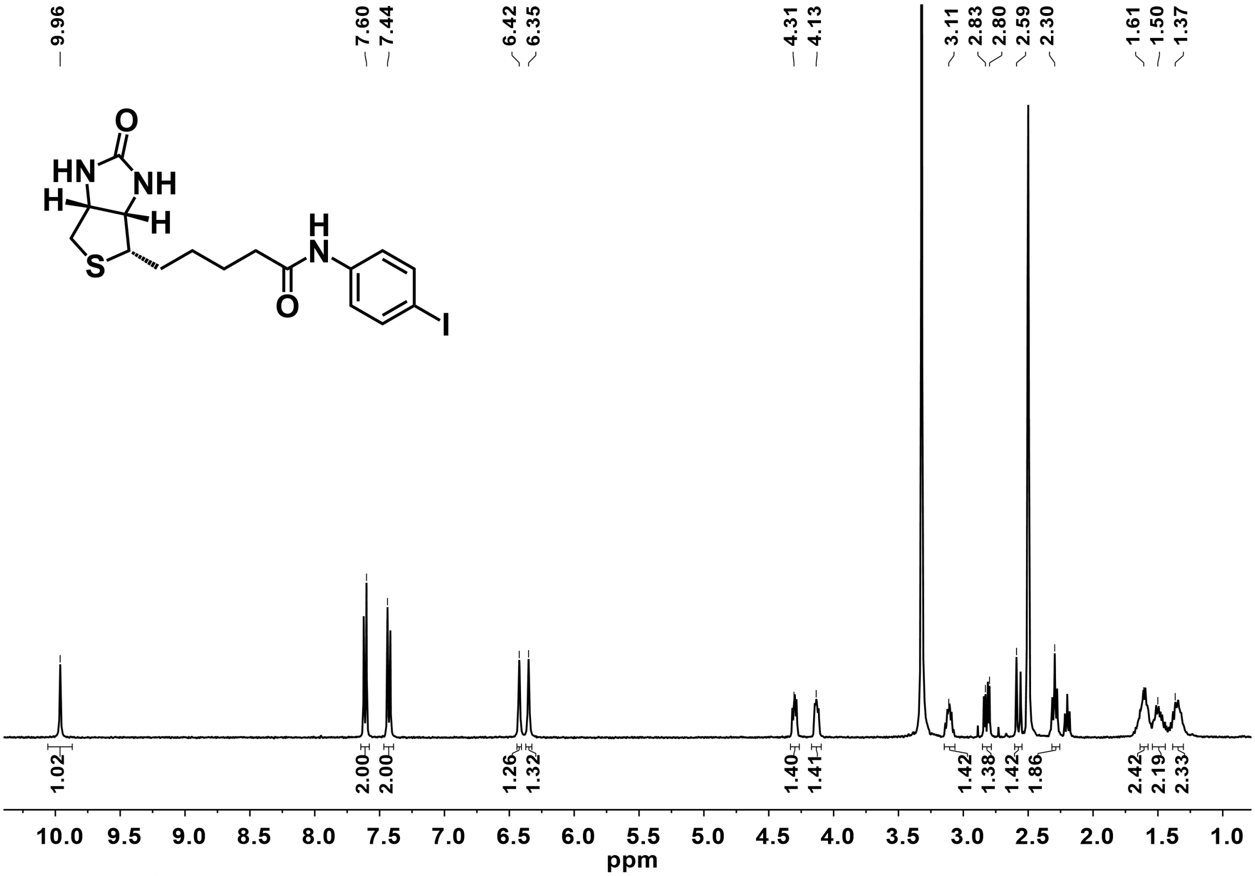


Figure S1. ^{1}H NMR spectrum of **SI-1** in DMSO-d_6 at 298 K.

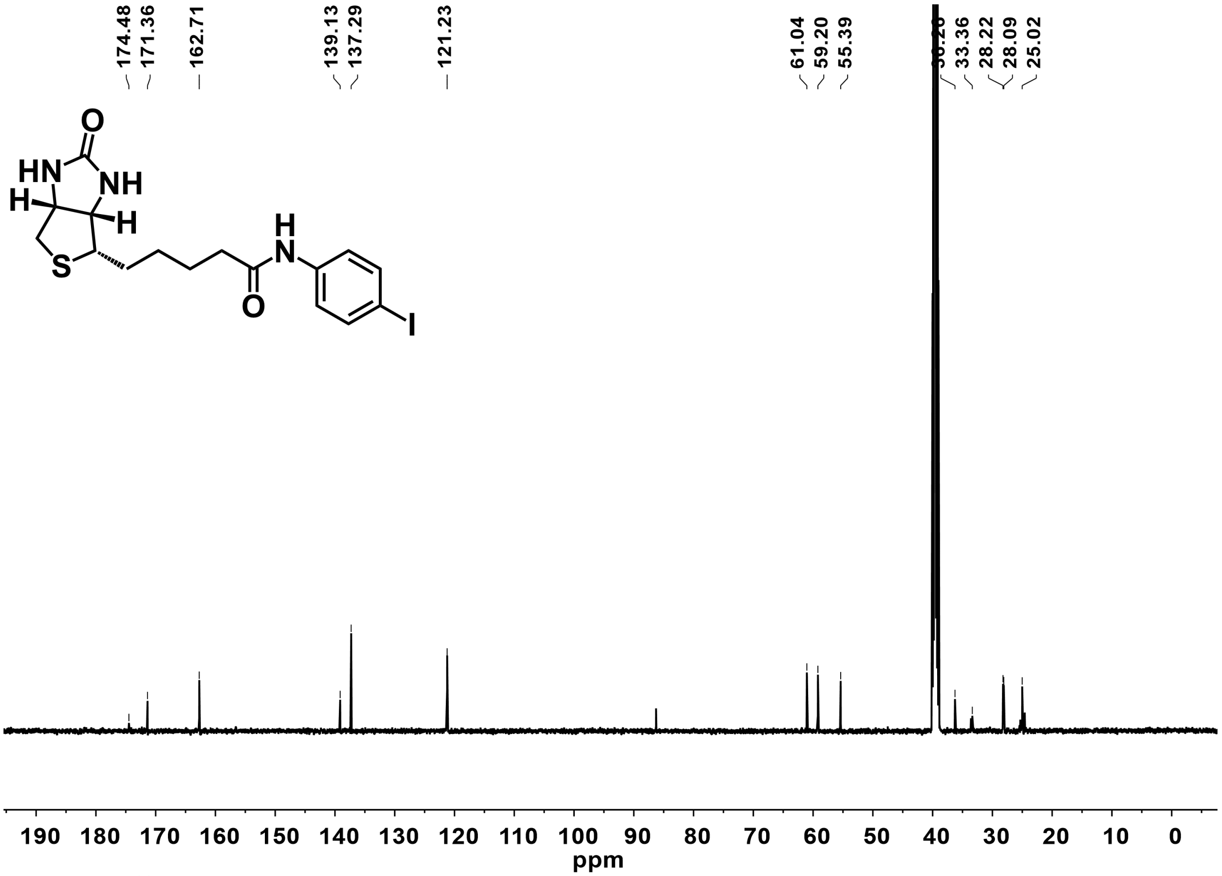
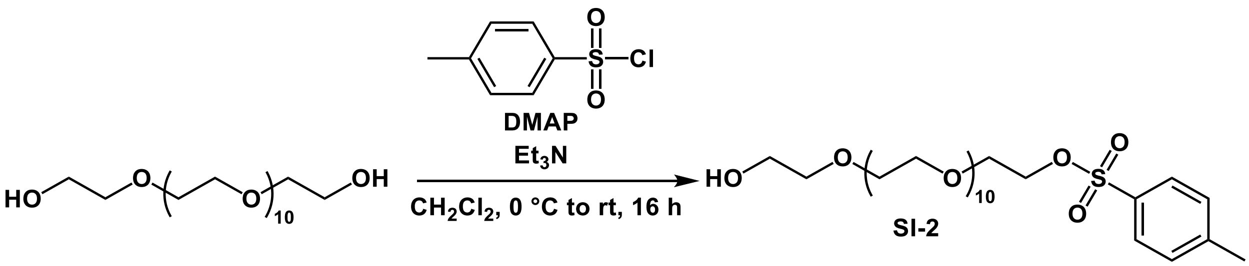


Figure S2. ^{13}C NMR spectrum of **SI-1** in DMSO-d_6 at 298 K.



A 2-neck round bottom flask was charged with a solution of poly(ethylene glycol) (577 mg, 1.05 mmol, 1.00 equiv) in dry CH_2Cl_2 (5 mL) under an atmosphere of Ar. To this solution was added 4-dimethylaminopyridine (26 mg, 0.21 mmol, 0.20 equiv) under stirring, and then the temperature of the reaction mixture was lowered to 0 ˚C. A solution of tosyl chloride (141 mg, 0.740 mmol, 0.700 equiv) in CH_2Cl_2 (15 mL) was added dropwise to this solution, followed by dropwise addition of triethylamine (177 μL, 1.26 mmol, 1.20 equiv). The reaction mixture was allowed to warm to room temperature, and then stirred for an additional 16 h, at which point the reaction was diluted with water and the product was extracted three times with CH_2Cl_2. The organic layers were collected, dried over $MgSO_4$, and the solvent was removed under reduced pressure to afford the product as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, 1H, J = 8.3 Hz, H_{Ar}), 7.34 (d, 1H, J = 8.3 Hz, H_{Ar}), 4.19–4.10 (m, 2H), 3.70–3.62 (m, 44H), 3.00 (s, 2H), 2.45 (s, 3H) ppm.

^{13}C NMR (125 MHz, $CDCl_3$): δ 144.78, 133.01, 129.82, 127.99, 72.52, 70.57, 69.24, 68.69, 61.76, 21.66 ppm.

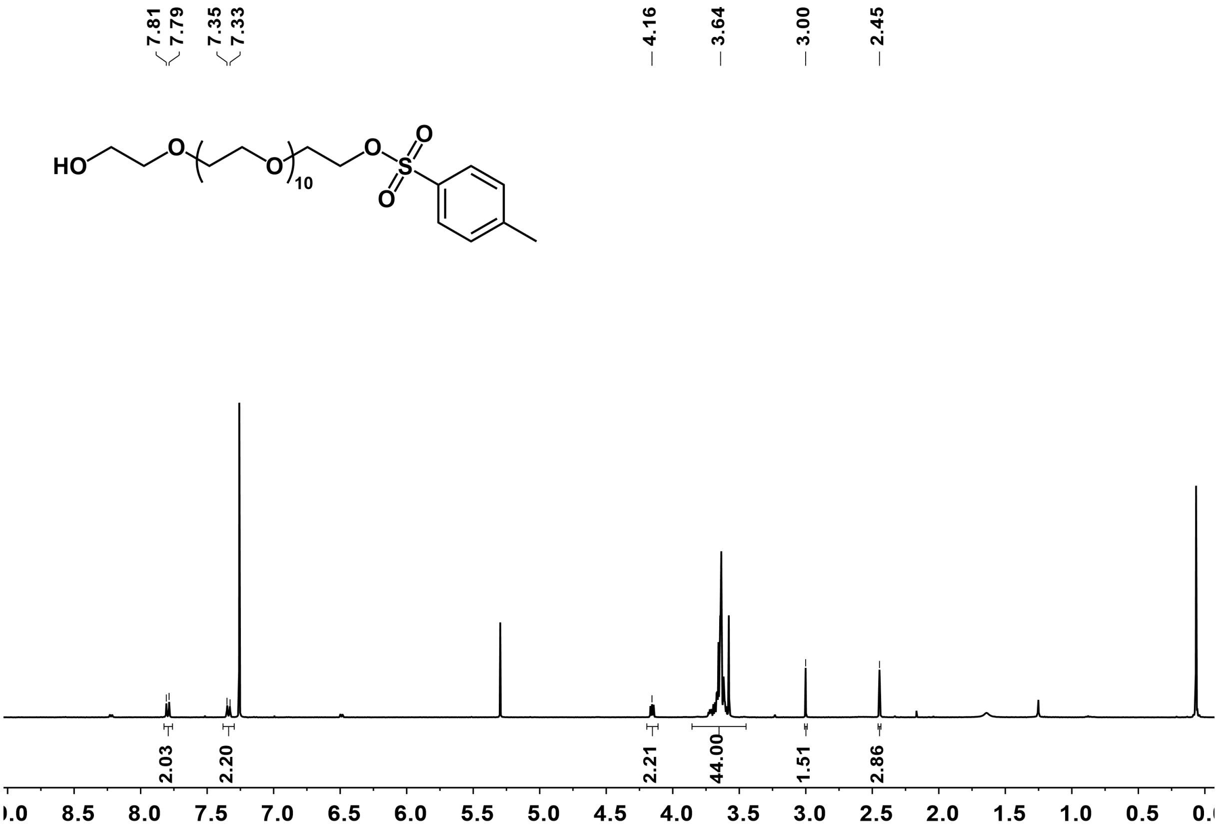


Figure S3. ^{1}H NMR spectrum of **SI-2** in $CDCl_3$ at 298 K.

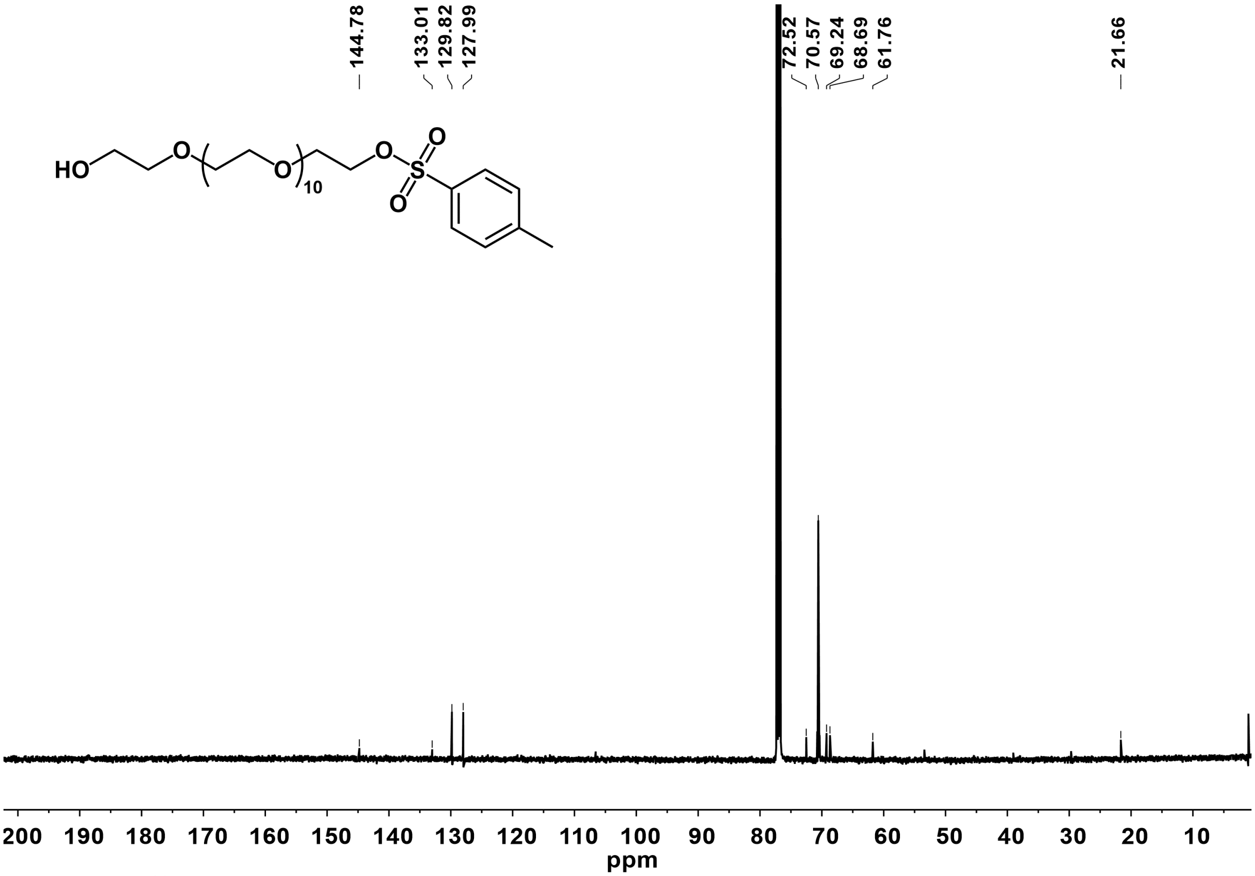
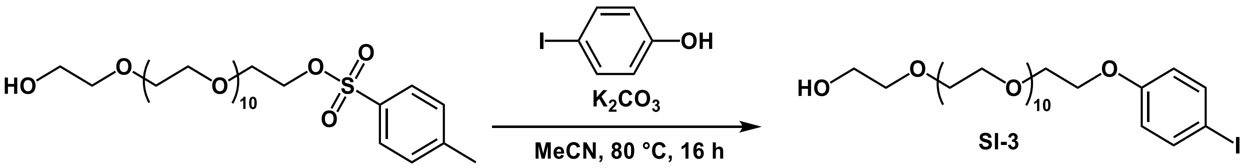


Figure S4. ^{13}C NMR spectrum of **SI-2** in $CDCl_3$ at 298 K.



A 2-neck round bottom flask was charged with a solution of **SI-2** (395 mg, 0.520 mmol, 1.00 equiv) and 4-iodophenol (164 mg, 0.750 mmol, 1.45 equiv) in dry MeCN (20 mL). To this solution was added potassium carbonate (427 mg, 3.09 mmol, 6.00 equiv) under stirring. The reaction mixture was stirred at 80 °C for 16 h, at which point the solvent was removed under reduced pressure to afford colorless solids, which were dissolved in ethyl acetate and washed with water. The organic layer was collected, dried over $MgSO_4$, and the solvent was removed under reduced pressure. The crude product was purified *via* column chromatography (90:10 $CHCl_3$:MeOH) to afford pure **SI-3** as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (d, 2H, *J* = 9.0 Hz, H_{Ar}), 6.69 (d, 2H, *J* = 9.0 Hz, H_{Ar}), 4.10–4.05 (m, 2H), 3.88–3.79 (m, 2H), 3.74–3.60 (m, 44H), 2.60 (t, 1H, t, *J* = 6.2 Hz) ppm.

^{13}C NMR (125 MHz, $CDCl_3$): δ 158.79, 138.27, 117.18, 83.02, 72.81, 70.65, 69.70, 67.65, 61.78 ppm.

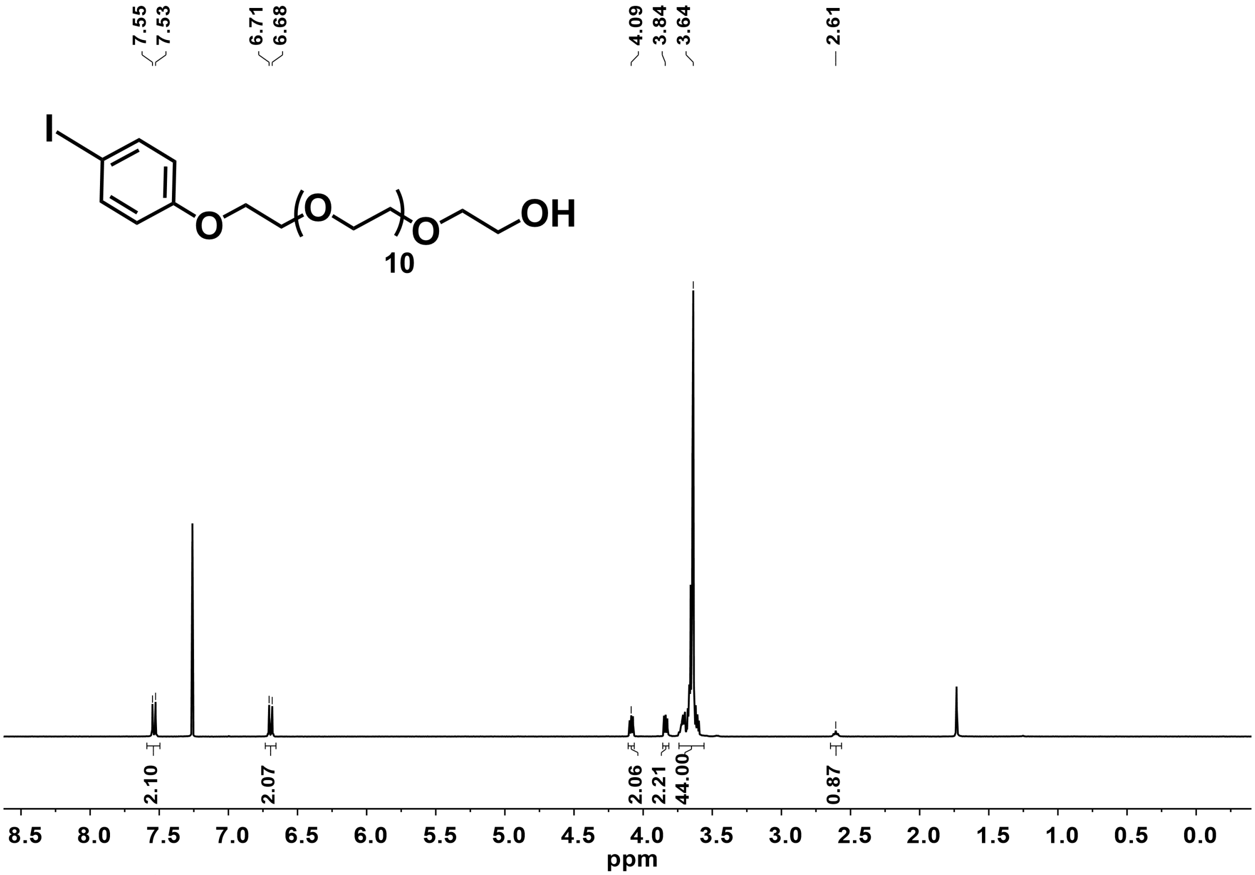


Figure S5. ^{1}H NMR spectrum of **SI-3** in $CDCl_3$ at 298 K.

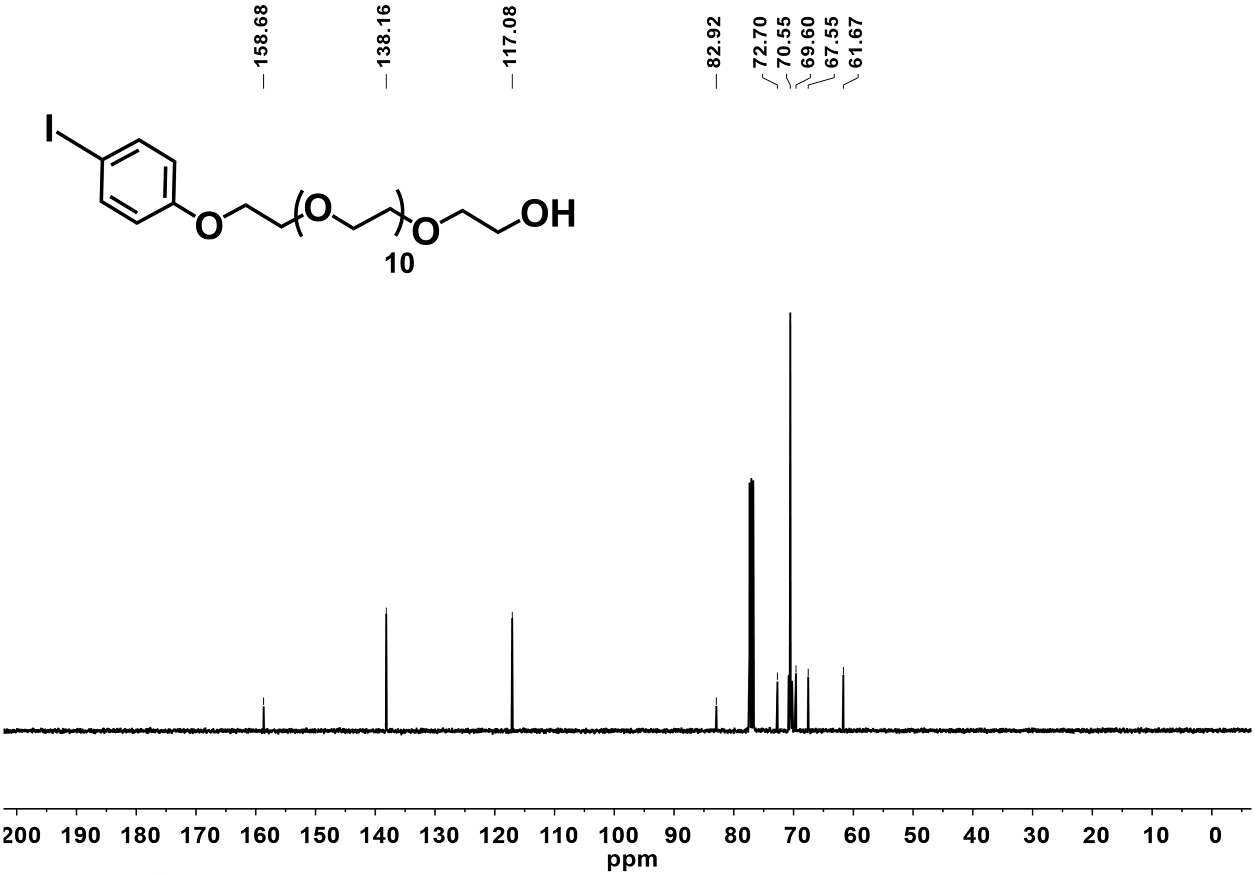
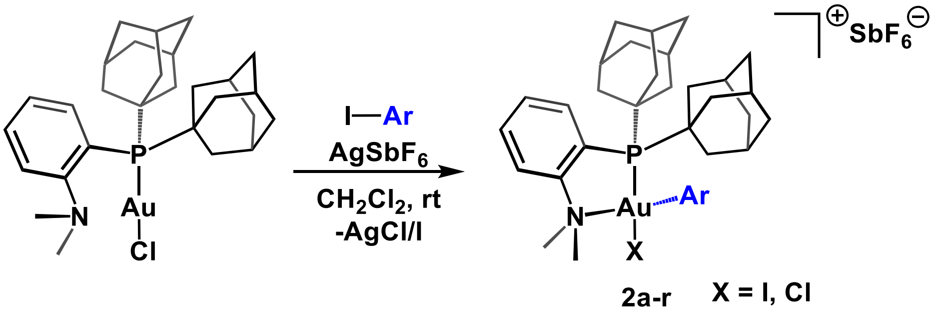


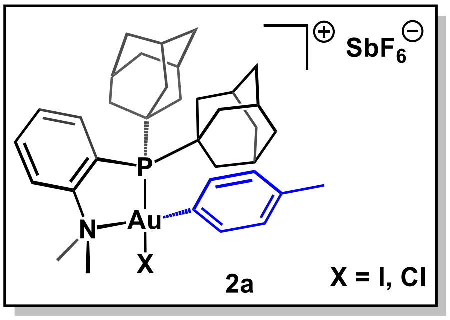
Figure S6. ^{13}C NMR spectrum of **SI-3** in $CDCl_3$ at 298 K.

General synthetic procedure for the preparation of [(Me-DalPhos)AuArX][SbF_6] oxidative addition complexes (X = Cl/I)



The $AgSbF_6$ and (Me-DalPhos)AuCl reagents were stored in the glovebox under an atmosphere of N_2 and then removed for use.

In the fume hood, $AgSbF_6$ was dissolved in DCM (2 mL) under protection from light, and the colorless solution was cooled to -20 °C. A DCM solution (2 mL) containing the aryliodide and (Me-DalPhos)AuCl reagents was prepared and also cooled to -20 °C. While both solutions were cold, the colorless aryliodide and (Me-DalPhos)AuCl solution was added in one portion to the solution of $AgSbF_6$, resulting in an immediate color change to bright yellow concomitant with precipitation of pale yellow solids. The reaction mixture was filtered through a pad of Celite to remove liberated AgX (X = Cl, I). Slow evaporation of solvent from the yellow filtrate over the course of 48 h at 25 °C resulted in saturation of the solution and the formation of yellow crystals. The supernatant was removed and the crystals were washed with C_6H_6 (2 × 3 mL), followed by *n*-pentane (2 × 3 mL), and then dried under reduced pressure to afford the [(Me-DalPhos)AuArCl][SbF_6] product as a yellow crystalline solid.



2a

Following the general procedure, (Me-DalPhos)AuCl (43 mg, 0.066 mmol, 1.0 equiv), $AgSbF_6$ (23 mg, 0.066 mmol, 1.0 equiv) and 4-iodotoluene (43 mg, 0.20 mmol, 3.0 equiv) were used. The [**2a**][SbF_6] salt was isolated as a yellow crystalline solid in 72% yield (47 mg, 0.045 mmol). This complex has been previously reported.[5]

^{1}H NMR (400 MHz, CD_3CN): δ 8.03 (m, 1H, H_{Ar}), 8.01–7.88 (m, 2H, H_{Ar}), 7.68 (m, 1H, H_{Ar}), 7.43 (d, 2H, *J* = 8.4 Hz, H_{Ar}), 7.14 (d, 2H, *J* = 8.4 Hz, H_{Ar}), 3.45 (s, 6H, $N(CH_3)_2$), 2.34 (s, 3H, Tolyl-CH_3), 2.33–2.25 (m, 6H, H_{Ad}), 2.03–1.98 (m, 12H, H_{Ad}), 1.80–1.66 (m, 12H, H_{Ad}) ppm.

$^{31}P\{^1H\}$ NMR (162 MHz, CD_3CN): δ 75.0 ppm.

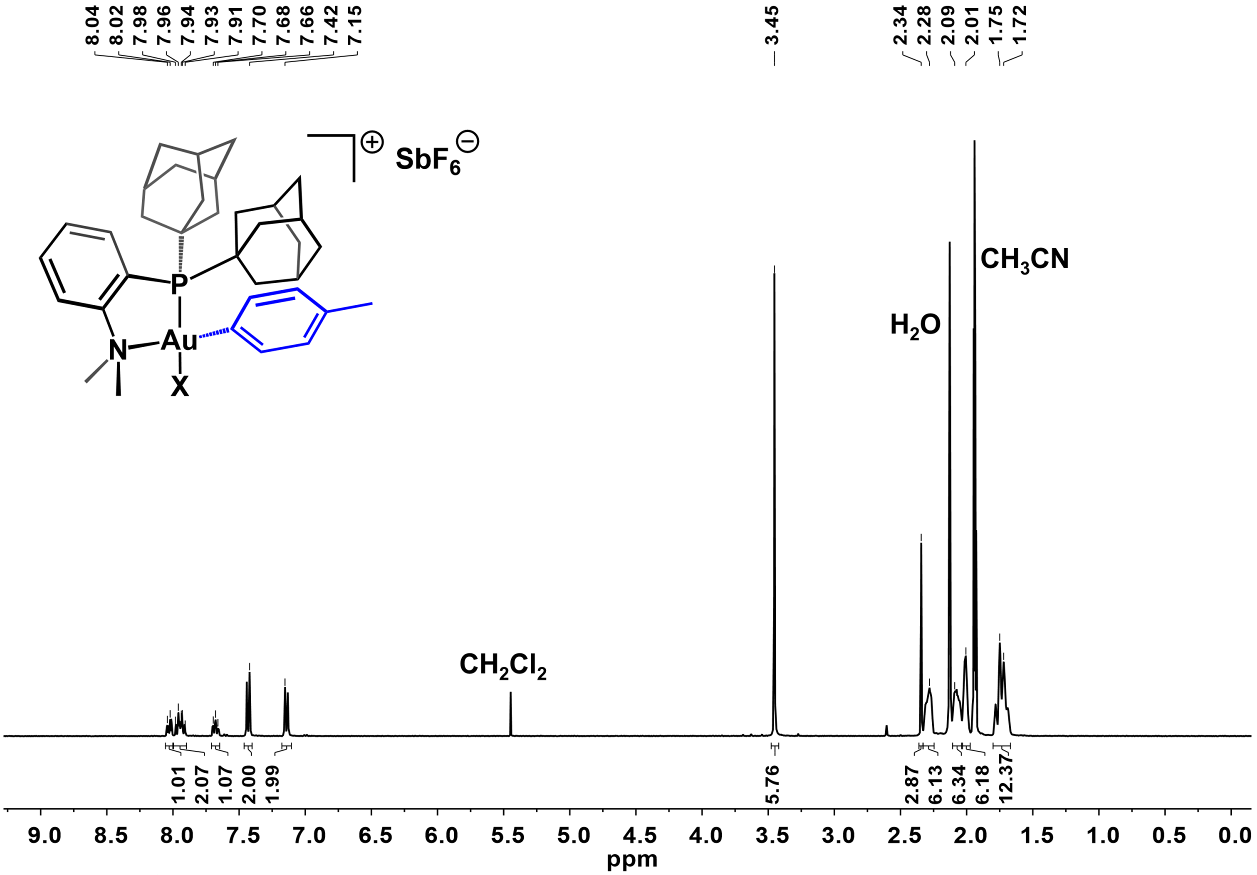


Figure S7. ^{1}H NMR spectrum of [**2a**][SbF_6] in CD_3CN at 298 K.

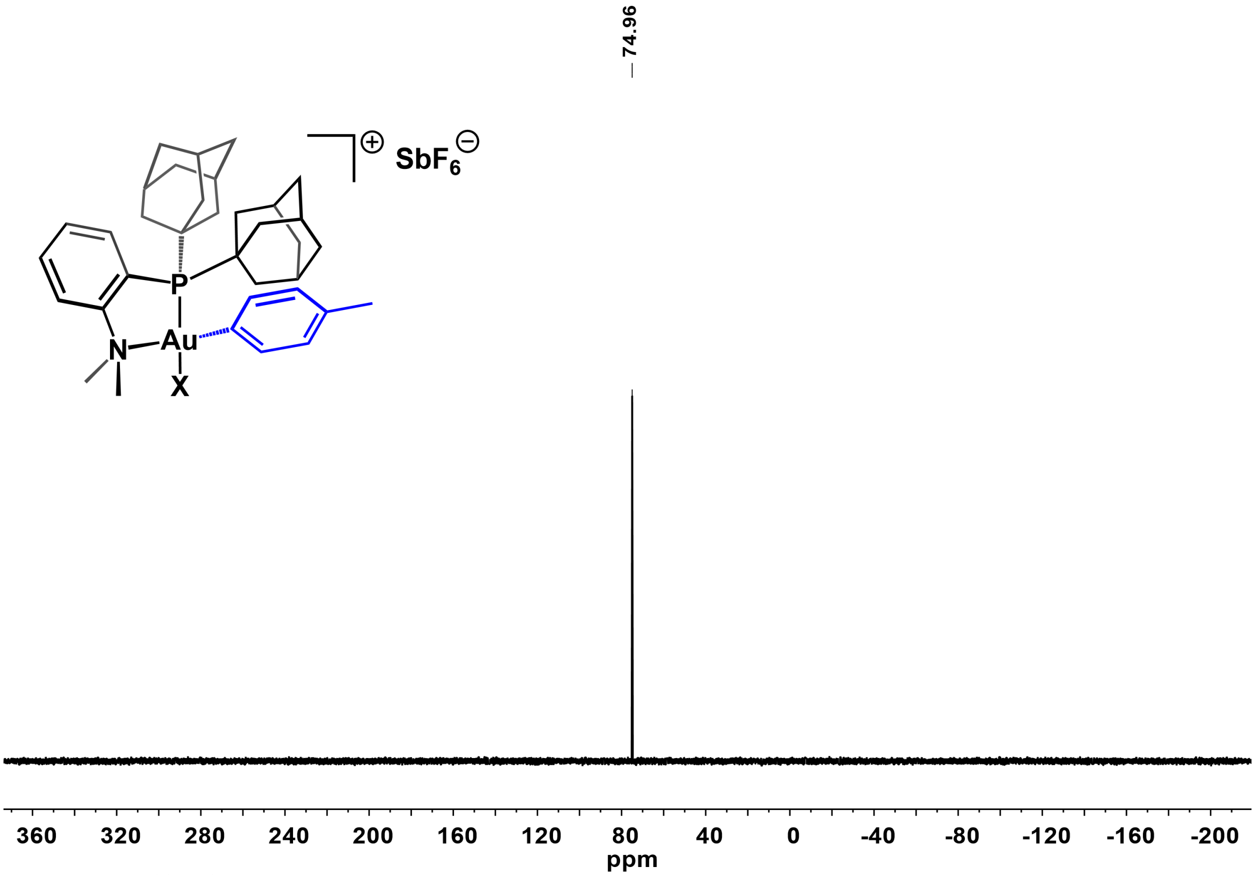
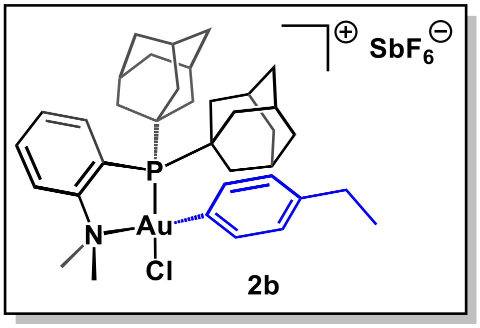


Figure S8. $^{31}P\{^1H\}$ NMR spectrum of [**2a**][SbF_6] in CD_3CN at 298 K.



2b

Following the general procedure, (Me-DalPhos)AuCl (30 mg, 0.046 mmol, 1.0 equiv), $AgSbF_6$ (16 mg, 0.046 mmol, 1.0 equiv) and 4-ethyliodobenzene (20 µL, 0.14 mmol, 3.0 equiv) were used. The [**2b**][SbF_6] salt was isolated as a yellow crystalline solid in 59% yield (27 mg, 0.027 mmol). A single crystal of suitable quality for an X-ray diffraction study was obtained using this procedure. The X-ray crystallographic analysis indicates 100% Cl occupancy (see section V for crystallographic details).

^{1}H NMR (400 MHz, CD_3CN): δ 8.03 (m, 1H, H_{Ar} 8.00–7.89 (m, 2H, H_{Ar}), 7.69 (m, 1H, H_{Ar}), 7.46 (d, 2H, J = 8.4, H_{Ar}), 7.17 (d, 2H, J = 8.2, H_{Ar}), 3.45 (s, 6H, $N(CH_3)_2$), 2.65 (q, 2H, J = 7.6 Hz, $-CH_2CH_3$), 2.28 (m, 6H, H_{Ad}), 2.11–2.08 (s, 6H, H_{Ad}) 2.04–1.99 (s, 6H, H_{Ad}), 1.73 (m, 12H, H_{Ad}), 1.23 (t, 3H, J = 7.6, $-CH_2CH_3$) ppm.

^{31}P{^{1}H} NMR (162 MHz, CD_3CN): δ 74.9 ppm.

ESI-MS(+): 768.33 (calc'd 768.33) *m/z*.
Note this sample was run in the presence of formic acid, and as a result, the [(Me-DalPhos)Au(*p*-ethylbenzene)OCHO]$^+$ ion is observed ($C_{37}H_{50}NO_2PAu$).

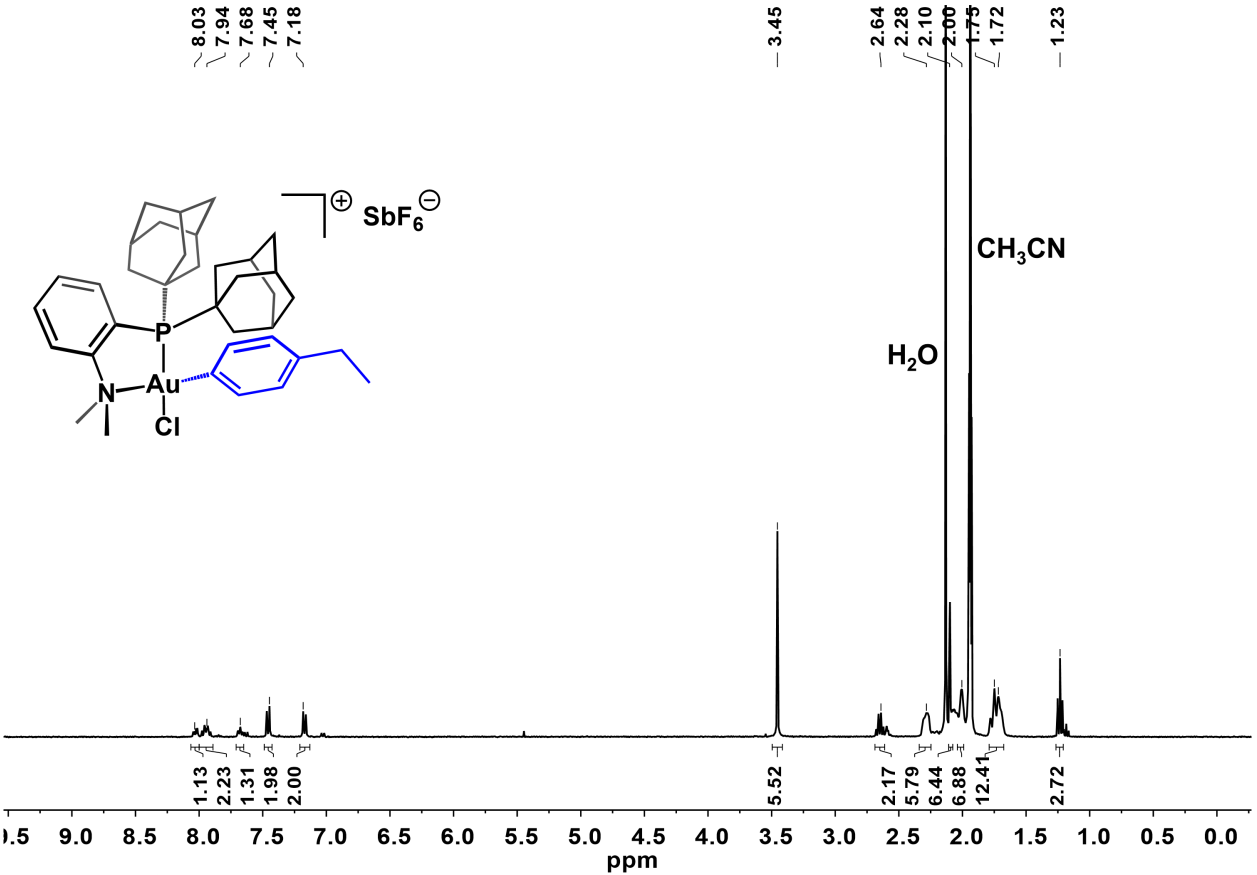


Figure S9. ^{1}H NMR spectrum of [**2b**][SbF_6] in CD_3CN at 298 K.

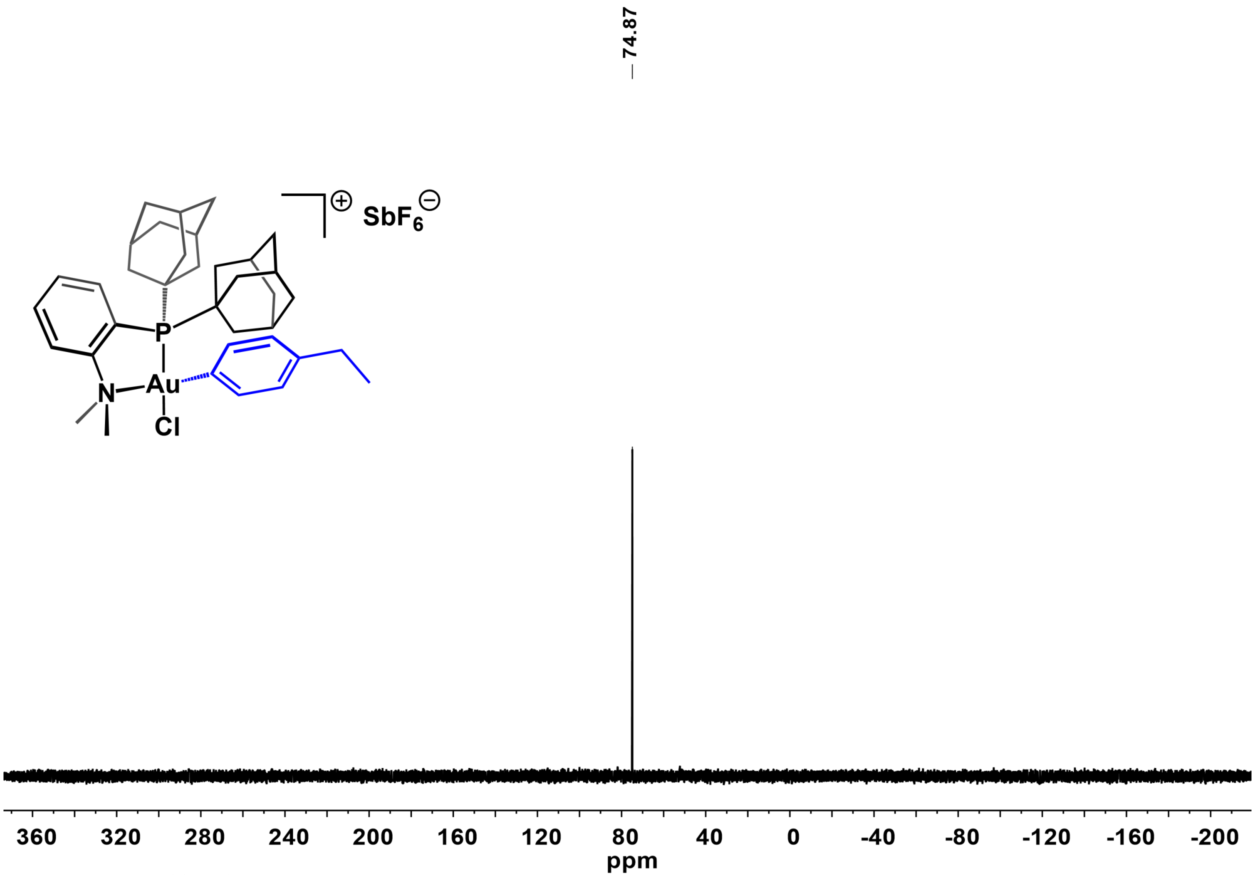


Figure S10. $^{31}P\{^{1}H\}$ NMR spectrum of [**2b**][SbF_6] in CD_3CN at 298 K.

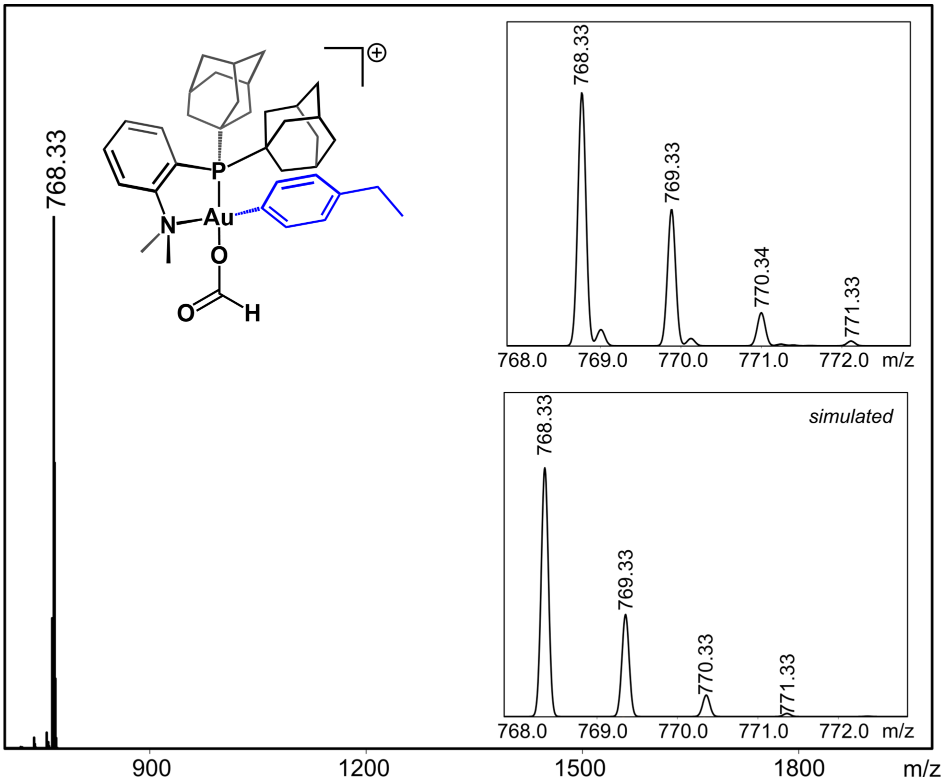
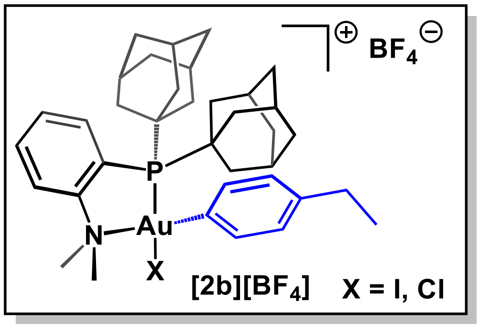


Figure S11. ESI-MS(+) of **2b**. Note this sample was run in the presence of formic acid, resulting in Cl^-/$OCHO^-$ exchange.



[**2b**][BF$_4$]

In the fume hood, a solution of AgBF$_4$ (9 mg, 0.05 mmol, 1 equiv) in DCM (2 mL) was prepared under protection from light, and then cooled to -20 °C. A DCM solution (2 mL) containing 4-ethyliodobenzene (20 μL, 0.14 mmol, 3.0 equiv) and (Me-DalPhos)AuCl (30 mg, 0.046 mmol, 1.0 equiv) reagents was prepared and also cooled to -20 °C. While both solutions were cold, the colorless 4-ethyliodobenzene and (Me-DalPhos)AuCl solution was added in one portion to the solution of AgBF$_4$, and the reaction mixture was sonicated for 2 min, during which time the solution became yellow concomitant with the precipitation of pale yellow precipitate. The resulting suspension was filtered through a pad of Celite, and the filtrate was dried *in vacuo* to give a pale-yellow powder. The solids were washed with C$_6$H$_6$ (2 × 3 mL), followed by *n*-pentane (2 × 3 mL), and then dried under reduced pressure to afford [**2b**][BF$_4$] as a pale yellow powder in 86% yield (36 mg, 0.043 mmol).

^{1}H NMR (400 MHz, CD$_3$CN): δ 8.05–8.01 (m, 1H, H$_{Ar}$), 7.99–7.92 (m, 2H, H$_{Ar}$), 7.73–7.67 (m, 1H), 7.46 (d, 2H, d, J = 8.4 Hz), 7.17 (d, 2H, J = 8.2 Hz), 3.45 (s, 6H, N(CH_3)$_2$), 2.65 (q, 2H, J = 7.7 Hz, -CH_2CH$_3$), 2.29 (s, 6H, H$_{Ad}$), 2.10 (s, 6H, H$_{Ad}$), 2.01 (s, 6H, H$_{Ad}$), 1.75 (s, 12H, H$_{Ad}$), 1.23 (t, 3H, J = 7.6 Hz, -CH$_2$CH_3) ppm.

^{31}P{^{1}H} NMR (162 MHz, CD$_3$CN): δ 75.7 ppm.

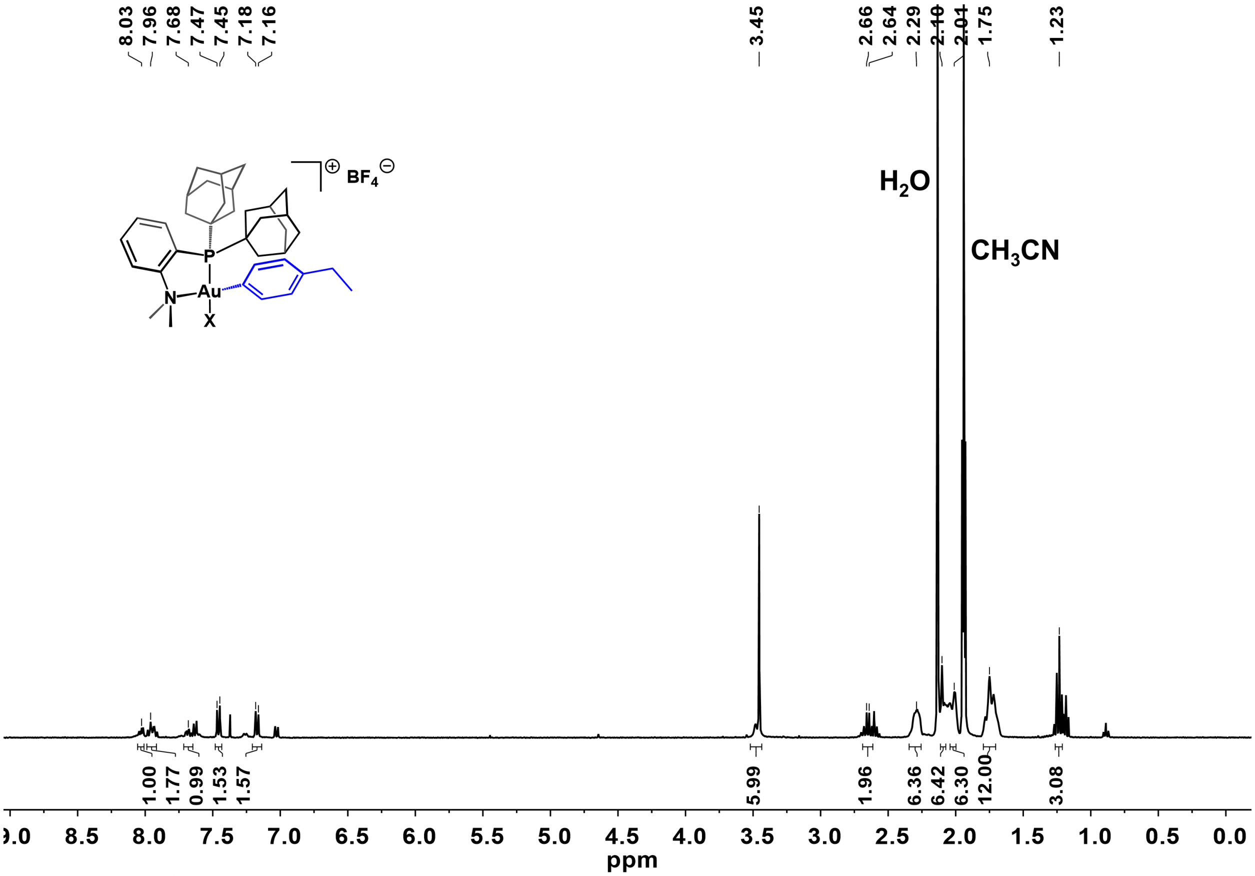


Figure S12. ^{1}H NMR spectrum of [**2b**][BF$_4$] in CD$_3$CN at 298 K.

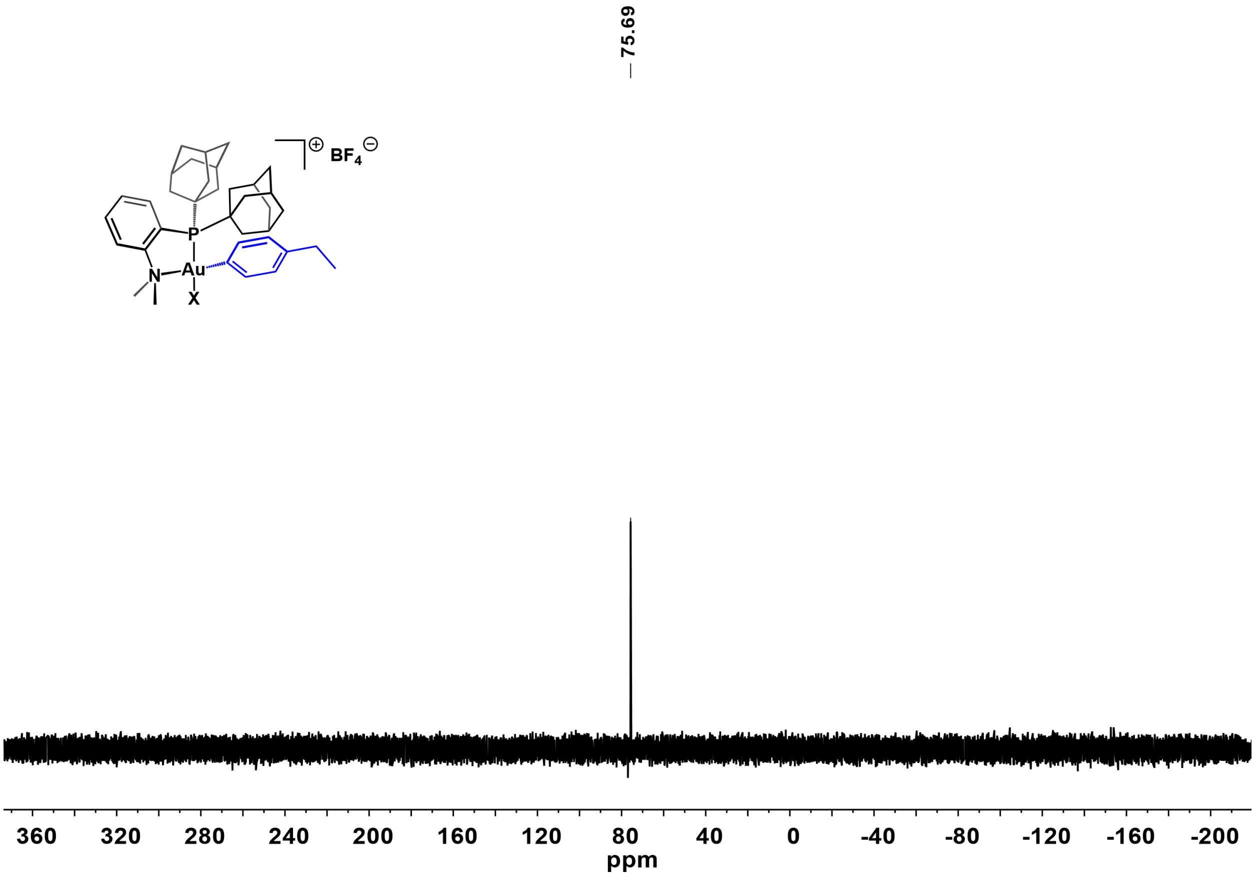
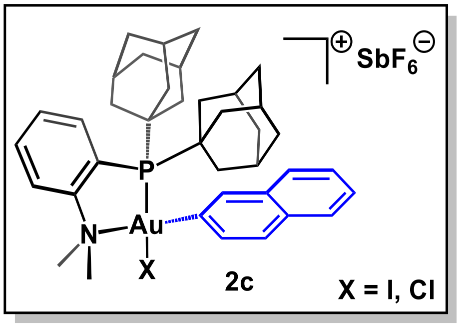


Figure S13. ^{31}P{^{1}H} NMR spectrum of [**2b**][BF$_4$] in CD$_3$CN at 298 K.



2c

Following the general procedure, (Me-DalPhos)AuCl (30 mg, 0.046 mmol, 1.0 equiv), $AgSbF_6$ (16 mg, 0.046 mmol, 1.0 equiv) and 2-iodonaphthalene (35 µL, 0.14 mmol, 3.0 equiv) were used. The [**2c**][SbF_6] salt was isolated as a yellow crystalline solid in 64% yield (30 mg, 0.029 mmol). A single crystal of suitable quality for an X-ray diffraction study was obtained using this procedure (see section V for crystallographic details).

^{1}H NMR (400 MHz, CD_3CN): δ 8.10 (m, 1H, H_{Ar}), 8.06 (m, 1H, H_{Ar}), 8.01–7.89 (m, 3H, H_{Ar}), 7.84 (m, 2H, H_{Ar}), 7.75–7.66 (m, 2H, H_{Ar}), 7.57 (m, 2H, H_{Ar}), 3.51 (s, 6H, $N(CH_3)_2$), 2.35 (m, 3H, H_{Ad}), 2.29–2.25 (m, 3H, H_{Ad}), 2.15 (m, 3H, H_{Ad}), 2.02 (m, 10H, H_{Ad}), 1.84–1.61 (m, 14H, H_{Ad}) ppm.

^{31}P{^{1}H} NMR (162 MHz, CD_3CN): δ 76.1 ppm.

ESI-MS(+): 780.21 (calc'd 780.28) *m/z* ($C_{38}H_{47}ClNPAu$).

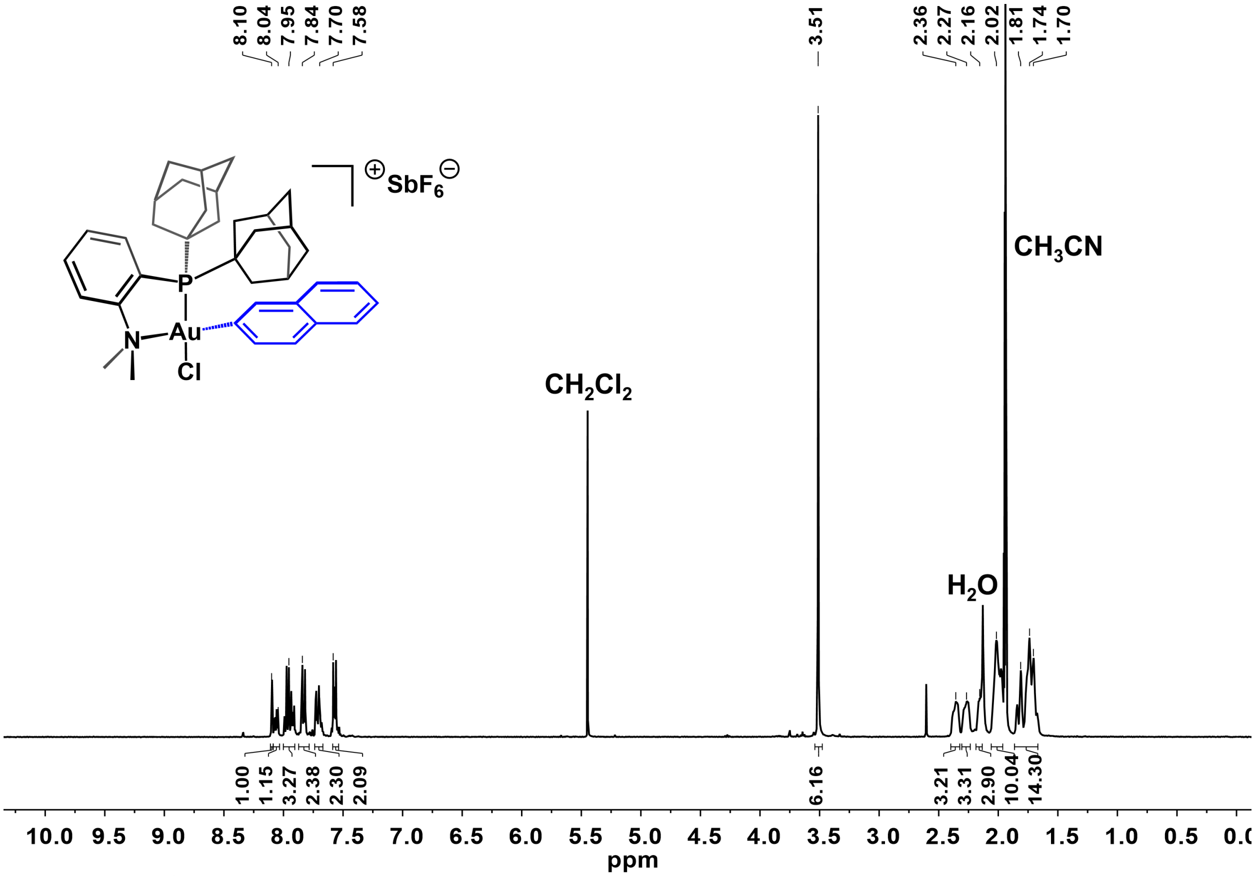


Figure S14. ^{1}H NMR spectrum of **2c** in CD_3CN at 298 K.

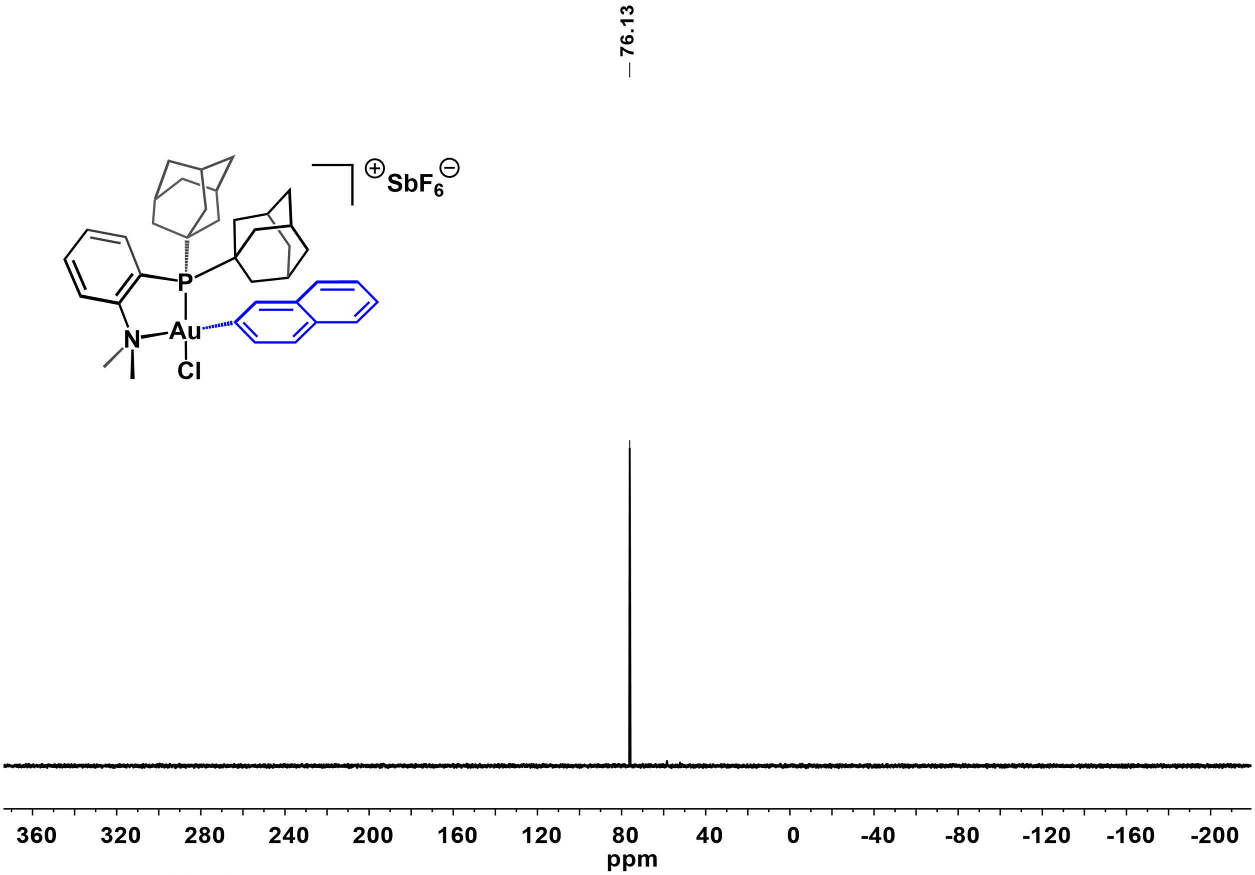


Figure S15. $^{31}P\{^1H\}$ NMR spectrum of **2c** in CD_3CN at 298 K.

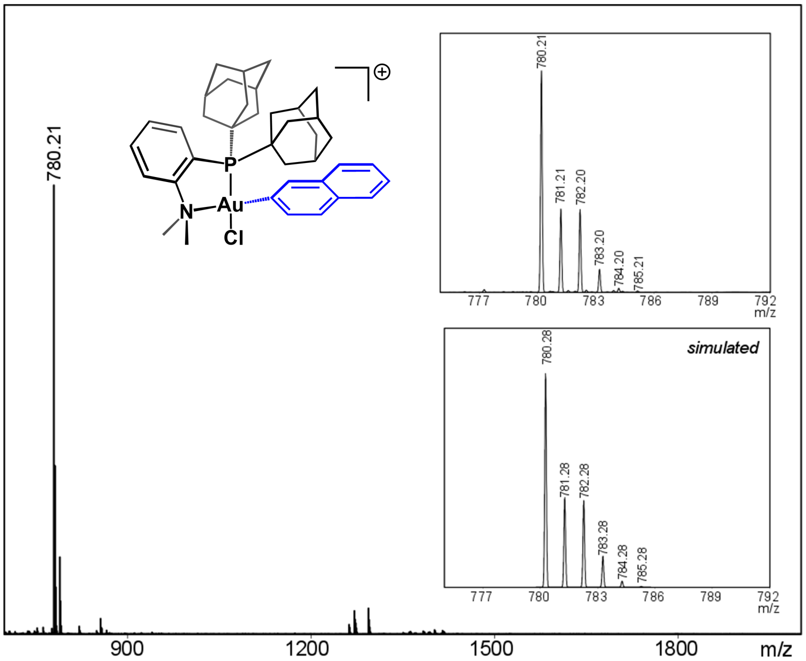
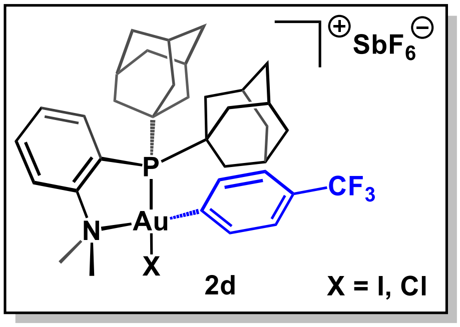


Figure S16. ESI-MS(+) of **2c**.



2d

Following the general procedure, (Me-DalPhos)AuCl (22 mg, 0.034 mmol, 1.0 equiv), $AgSbF_6$ (12 mg, 0.034 mmol, 1.0 equiv) and 4-iodobenzotrifluoride (25 µL, 0.17 mmol, 5.0 equiv) were used. The [**2d**][SbF_6] salt was isolated as a yellow crystalline solid in 60% yield (21 mg, 0.020 mmol). A single crystal of suitable quality for an X-ray diffraction study was obtained using this procedure (see section V for crystallographic details).

^{1}H NMR (400 MHz, CD_3CN): δ 8.08–8.01 (m, 1H, H_{Ar}), 8.00–7.90 (m, 2H, H_{Ar}), 7.82 (d, *J* = 8.3 Hz, 2H, H_{Ar}), 7.74–7.66 (m, 1H, H_{Ar}), 7.64 (d, *J* = 8.3 Hz, 2H, H_{Ar}), 3.50 (s, 6H, $N(CH_3)_2$), 2.36–2.25 (m, 6H, H_{Ad}), 2.02 (m, 11H, H_{Ad}), 1.74 (m, 13H, H_{Ad}) ppm.

^{19}F NMR (376 MHz, CD_3CN): δ -63.0 ppm.

^{31}P{^{1}H} NMR (162 MHz, CD_3CN): δ 77.6 ppm.

ESI-MS(+): 798.17 (calc'd 798.25) *m/z* ($C_{35}H_{44}ClF_3NPAu$).

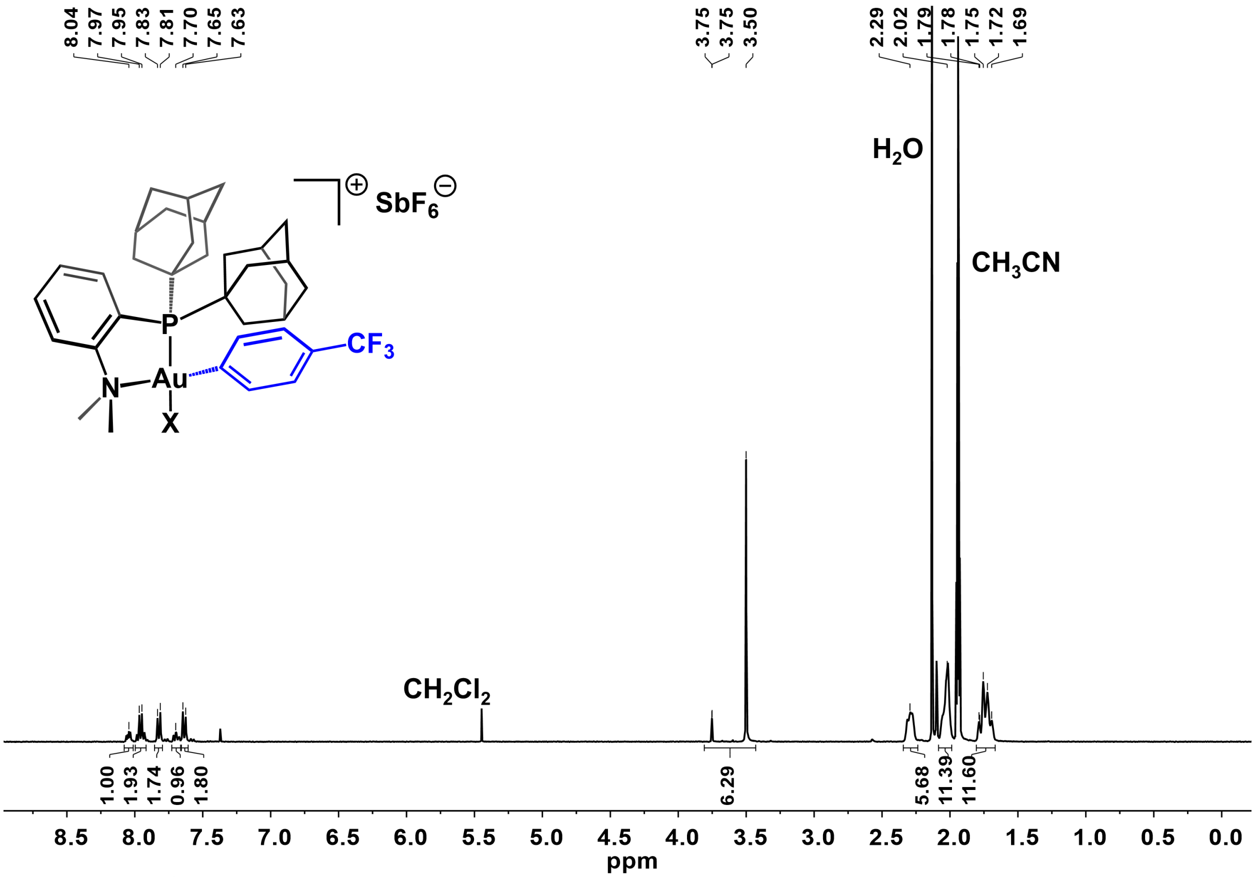


Figure S17. ^{1}H NMR spectrum of [**2d**][SbF_6] in CD_3CN at 298 K.

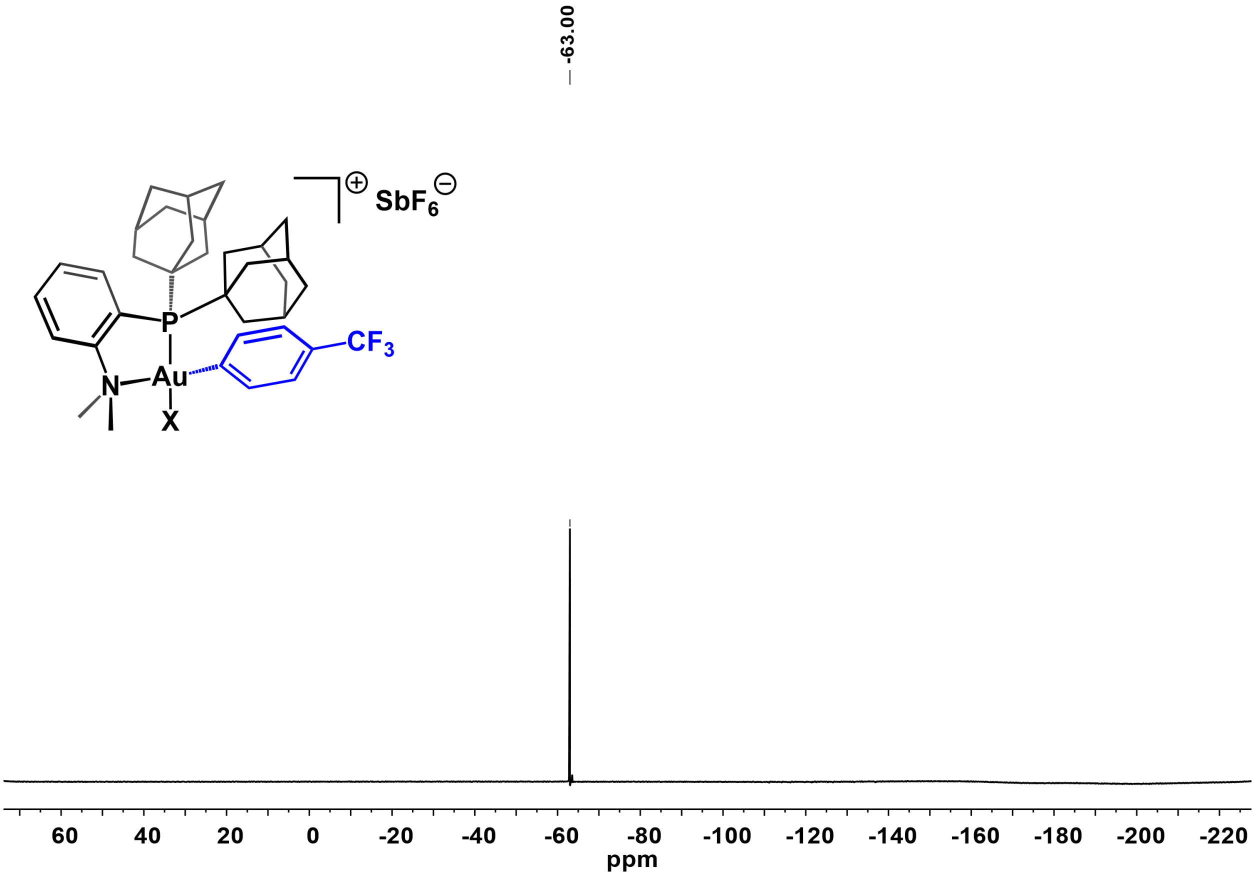


Figure S18. ^{19}F NMR spectrum of [**2d**][SbF$_6$] in CD$_3$CN at 298 K.

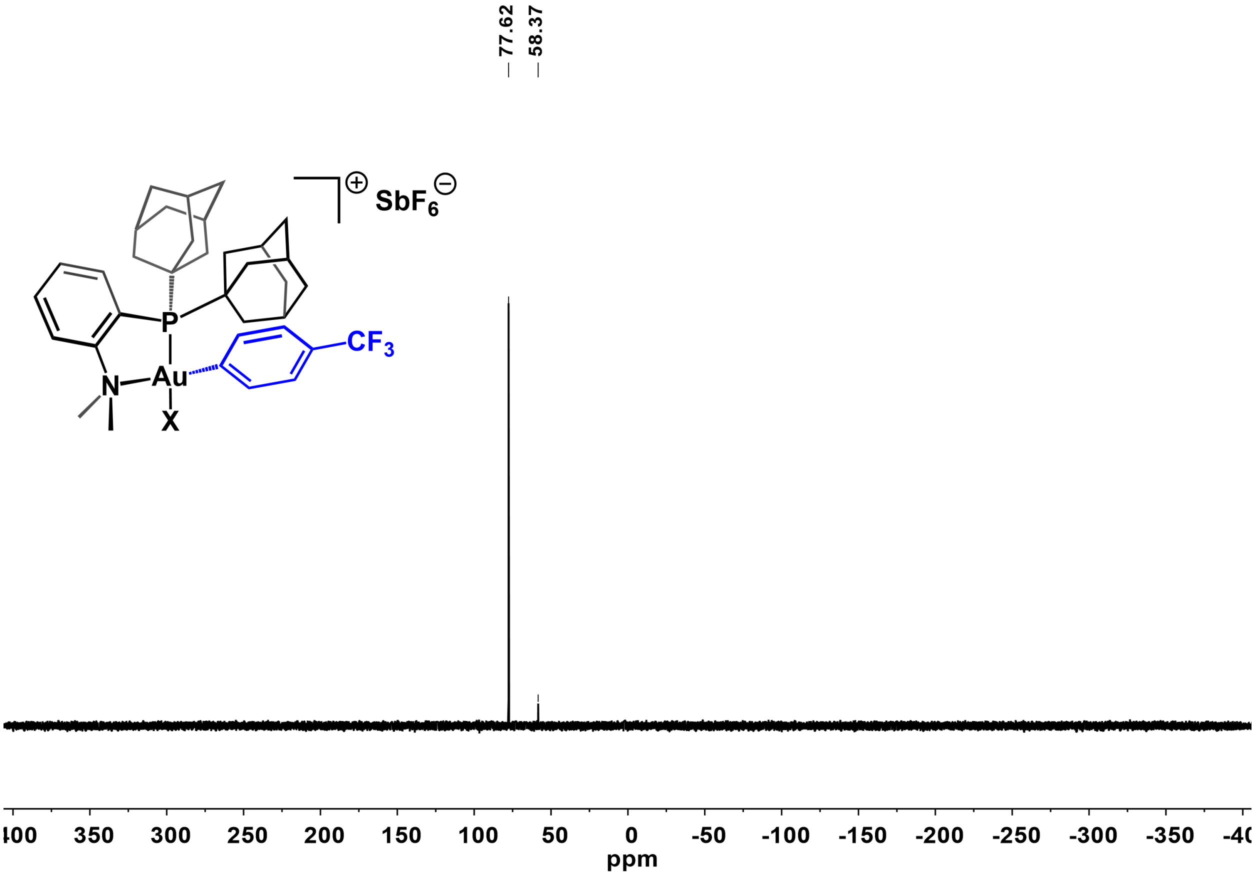


Figure S19. ^{31}P{^{1}H} NMR spectrum of [**2d**][SbF$_6$] in CD$_3$CN at 298 K. The signal at 58.3 ppm corresponds to the starting (Me-DalPhos)AuCl compound.

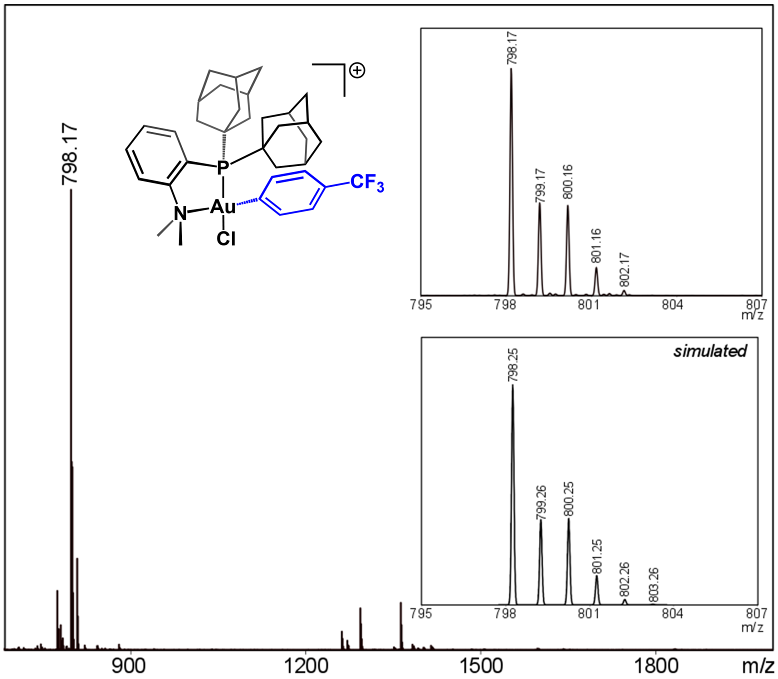
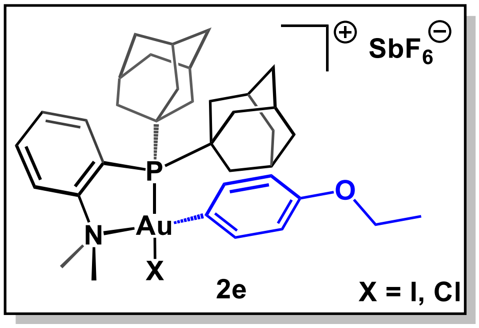


Figure S20. ESI-MS(+) of **2d**.



2e

In the fume hood, a solution of $AgSbF_6$ (12 mg, 0.034 mmol, 1.0 equiv) in DCM (2 mL) was prepared under protection from light, and then cooled to -20 °C. A DCM solution (2 mL) containing 4-iodophenetole (34 mg, 0.14 mmol, 3.0 equiv) and (Me-DalPhos)AuCl (30 mg, 0.046 mmol, 1.0 equiv) reagents was prepared and also cooled to -20 °C. While both solutions were cold, the colorless 4-iodophenetole and (Me-DalPhos)AuCl solution was added in one portion to the solution of $AgSbF_6$, at which point an immediate color change to yellow occurred concomitant with the precipitation of pale yellow precipitate. The resulting suspension was filtered through a pad of Celite, and the filtrate was dried *in vacuo* to give a pale-yellow powder. The solids were washed with C_6H_6 (2 x 3 mL), followed by *n*-pentane (2 x 3 mL), and then dried under reduced pressure to afford [**2e**][SbF_6] as a pale yellow powder in 85% yield (29 mg, 0.029 mmol).

^{1}H NMR (400 MHz, CD_3CN): δ 8.02 (m, 1H, H_{Ar}), 7.95 (m, 2H, H_{Ar}), 7.72–7.64 (m, 1H, H_{Ar}), 7.43 (d, 2H, *J* = 9.0 Hz), 6.92 (d, 2H, *J* = 8.9 Hz), 4.04 (q, 2H, *J* = 7.0 Hz, -CH_2CH_3), 3.46 (s, 6H, $N(CH_3)_2$), 2.29 (m, 6H, H_{Ad}), 2.12–1.98 (m, 12H, H_{Ad}), 1.73 (m, 12H, H_{Ad}), 1.37 (t, 3H, *J* = 7.0 Hz) ppm.

$^{31}P\{^1H\}$ NMR (162 MHz, CD_3CN): δ 75.1 ppm.

ESI-MS(+): 774.23 (calc'd 774.29) *m/z* ($C_{36}H_{49}ClNOPAu$).

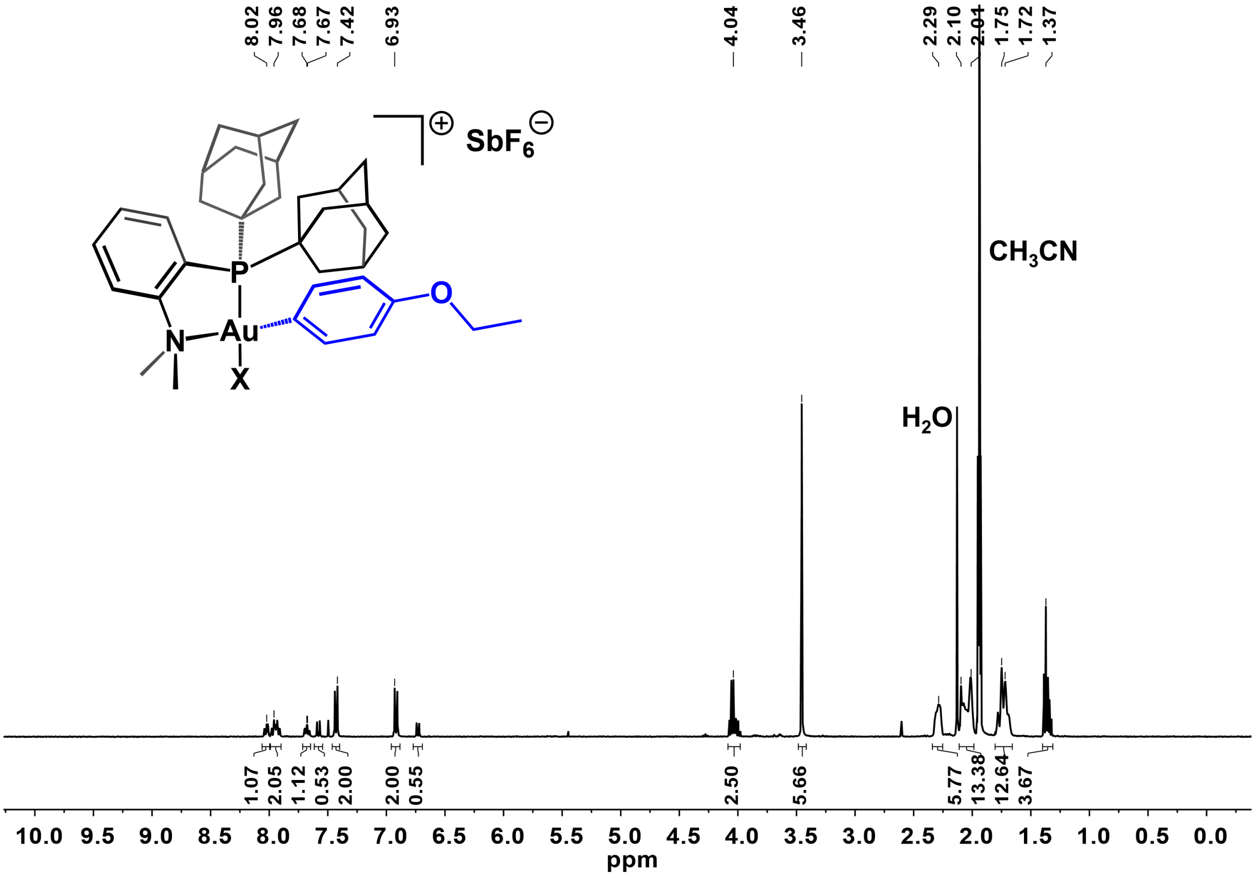


Figure S21. ^{1}H NMR spectrum of [**2e**][SbF_6] in CD_3CN at 298 K.

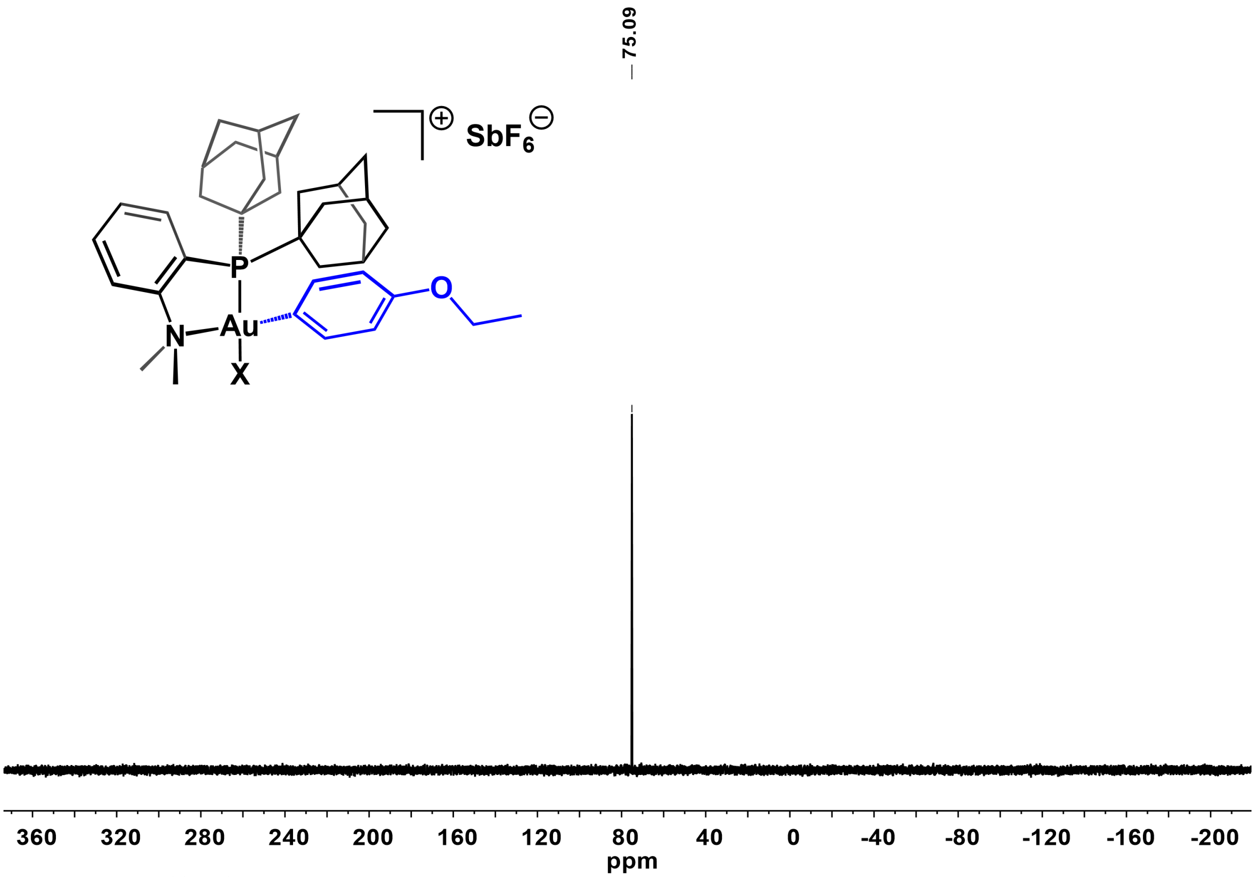


Figure S22. $^{31}P\{^{1}H\}$ NMR spectrum of [**2e**][SbF$_6$] in CD$_3$CN at 298 K.

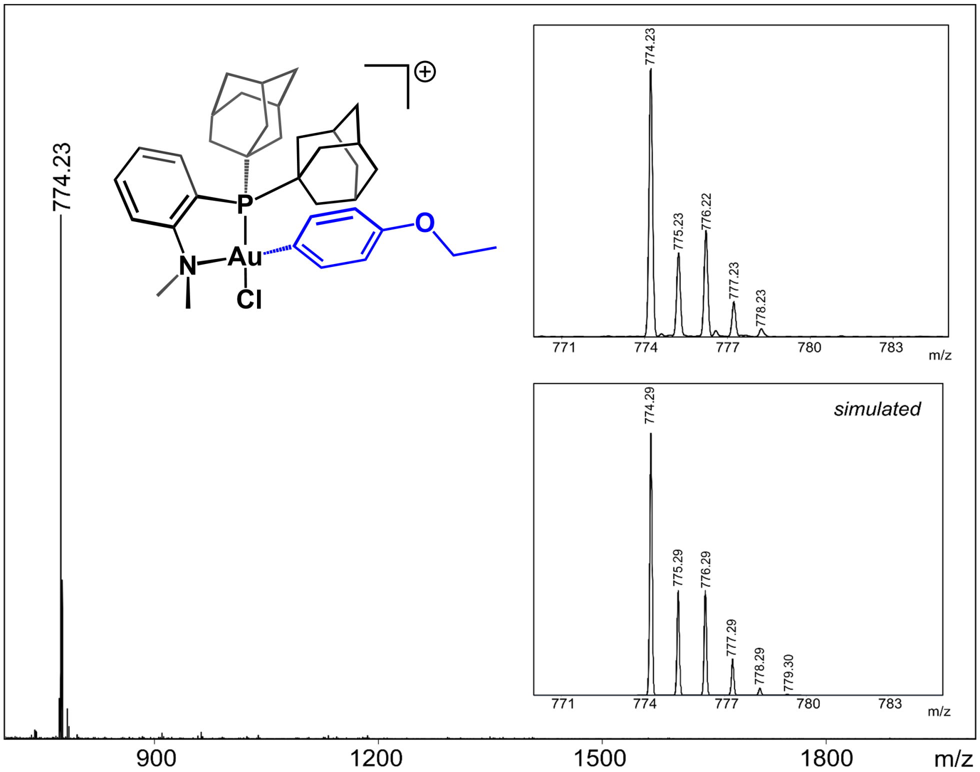
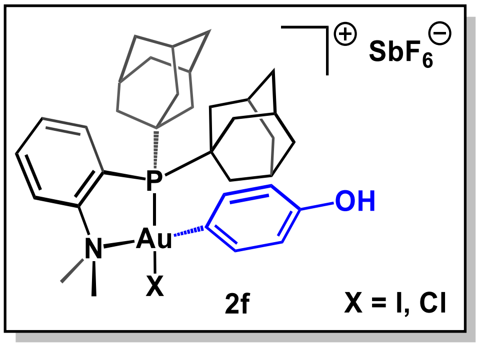


Figure S23. ESI-MS(+) of **2e**.



2f

Following the general procedure, (Me-DalPhos)AuCl (30 mg, 0.046 mmol, 1.0 equiv), $AgSbF_6$ (16 mg, 0.046 mmol, 1.0 equiv) and 4-iodophenol (31 mg, 0.14 mmol, 3.0 equiv) were used. The [**2f**][SbF_6] salt was isolated as an orange crystalline solid in 65% yield (29 mg, 0.030 mmol). A single crystal of suitable quality for an X-ray diffraction study was obtained using this workup (See section V for crystallographic details). Elem. Anal. (Calc'd) for [**2f**][SbF_6]·H_2O, $C_{34}H_{47}AuClF_6NO_2PSb$: C, 40.64 (40.78); H, 4.51 (4.73); N, 1.39 (1.40). Crystallographic analysis displays one co-crystallized water molecule for each [**2f**][SbF_6] salt complex (see section V).

^{1}H NMR (400 MHz, CD_3CN): δ 8.02 (m, 1H, H_{Ar}), 8.01–7.88 (m, 2H, H_{Ar}), 7.67 (m, 1H, H_{Ar}), 7.35 (d, 2H, J = 8.9 Hz, H_{Ar}), 6.83 (d, 1H, J = 8.7 Hz, H_{Ar}), 3.45 (s, 6H, $N(CH_3)_2$), 2.28 (m, 6H, H_{Ad}), 2.11–2.01 (m, 12H, H_{Ad}), 1.75 (m, 12H, H_{Ad}) ppm.

^{31}P{^{1}H} NMR (162 MHz, CD_3CN): δ 75.6 ppm.

ESI-MS(+): 746.15 (746.26) *m/z* ($C_{34}H_{44}Cl_2NPAu$).

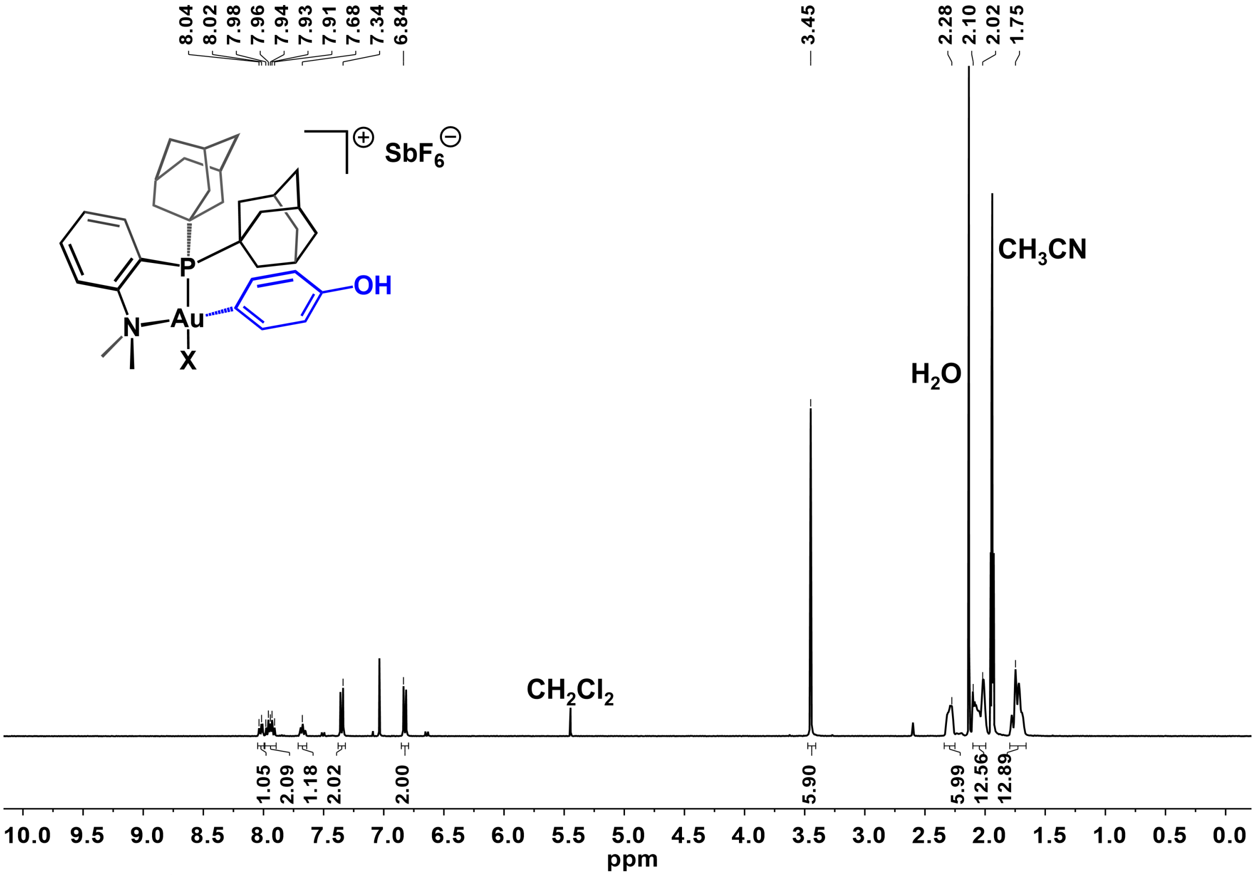


Figure S24. ^{1}H NMR spectrum of [**2f**][SbF6] in CD_3CN at 298 K.

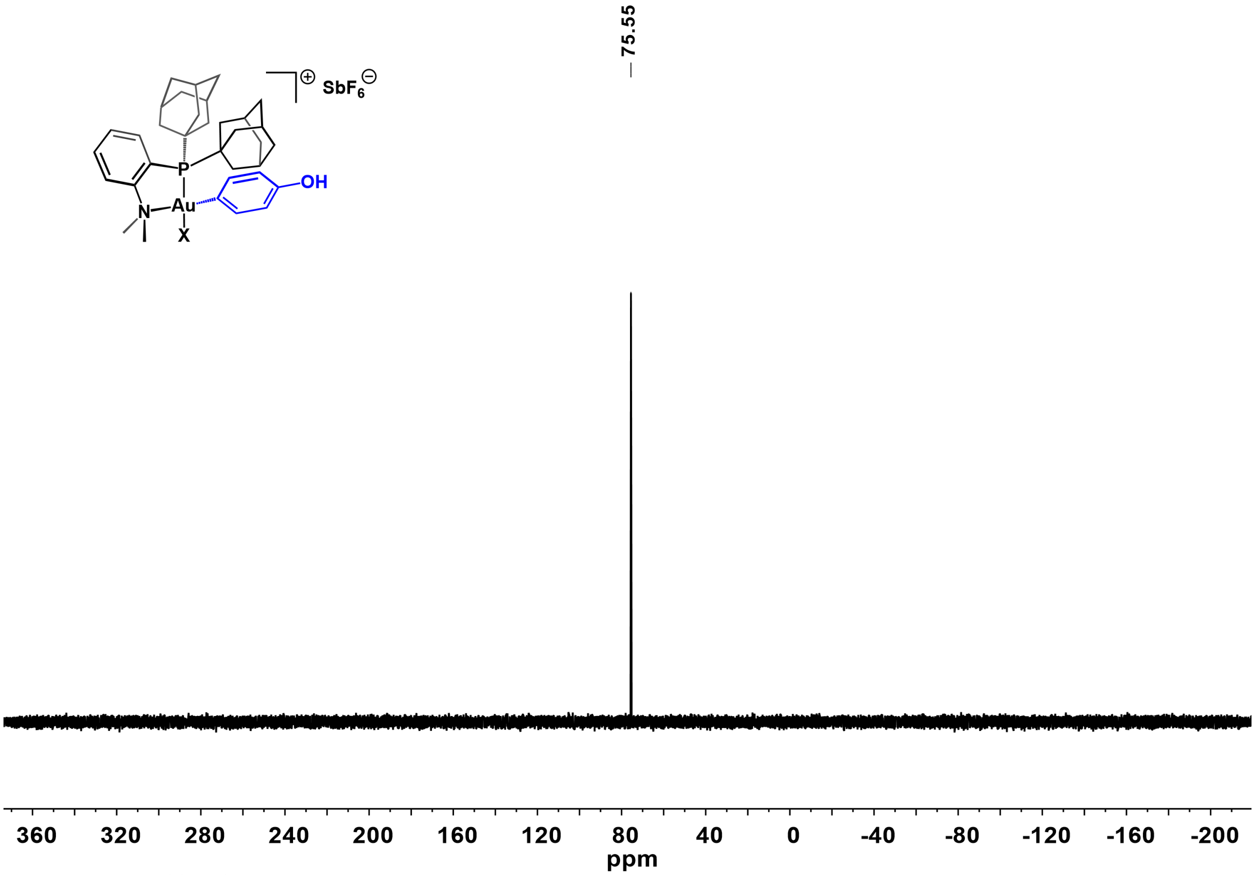


Figure S25. ^{31}P{^{1}H} NMR spectrum of [**2f**][SbF6] in CD$_3$CN at 298K.

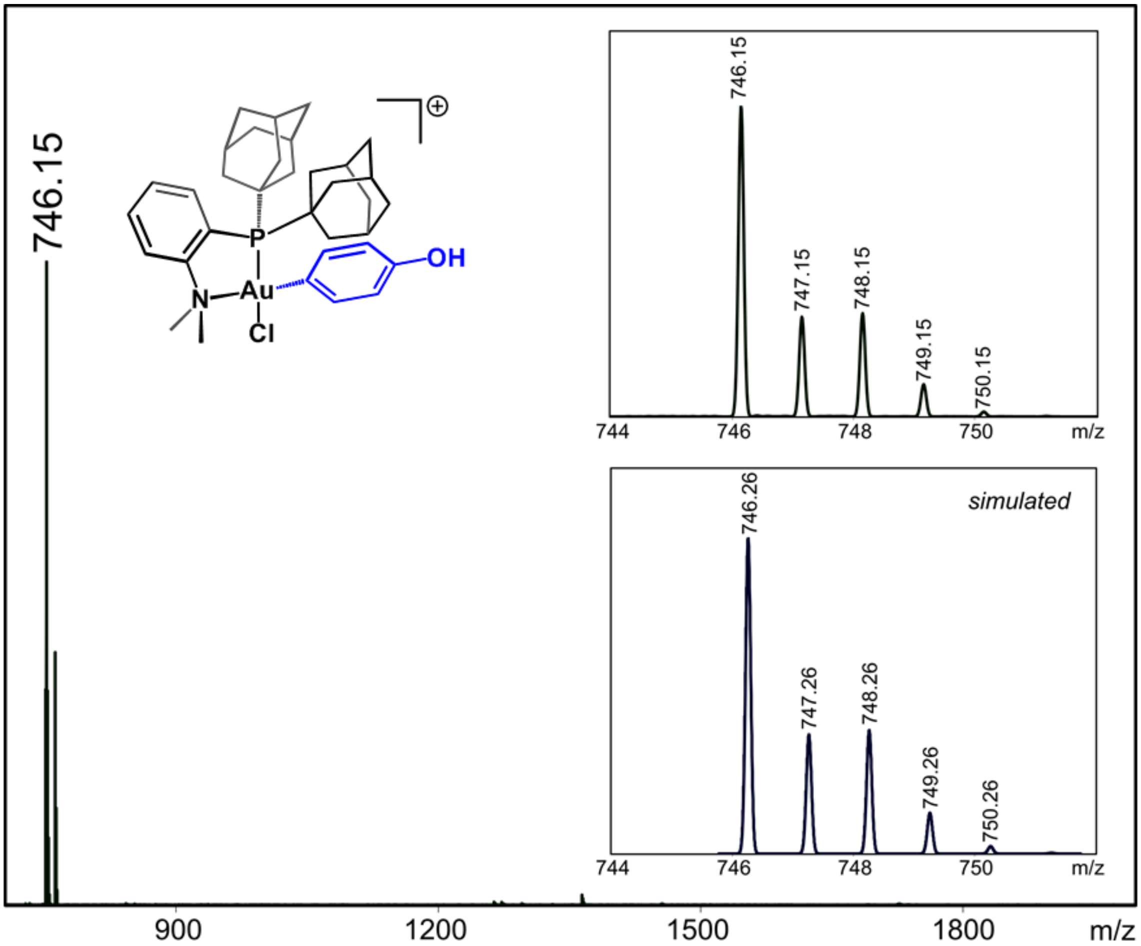
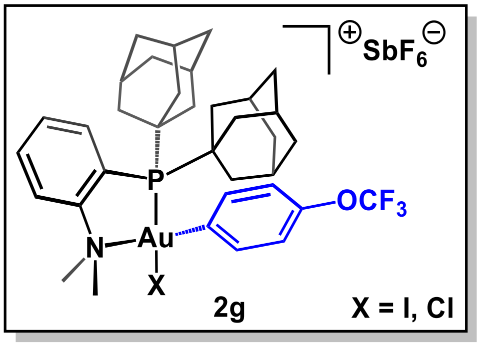


Figure S26. ESI-MS(+) of **2f**.



2g

Following the general procedure, (Me-DalPhos)AuCl (22 mg, 0.034 mmol, 1.0 equiv), $AgSbF_6$ (12 mg, 0.034 mmol, 1.0 equiv) and 4-(trifluoromethoxy)iodobenzene (27 µL, 0.17 mmol, 5.0 equiv) were used. The [**2g**][SbF_6] salt was isolated as a yellow crystalline solid in 51% yield (18 mg, 0.017 mmol). A single crystal of suitable quality for an X-ray diffraction study was obtained using this procedure (See section V for crystallographic details).

^{1}H NMR (400 MHz, CD_3CN): δ 8.04 (dd, *J* = 8.3, 3.9 Hz, 1H, H_{Ar}), 7.95 (m, 2H, H_{Ar}), 7.79–7.56 (m, 3H, H_{Ar}), 7.30 (d, *J* = 8.4 Hz, 2H, H_{Ar}), 3.49 (s, 6H, $N(CH_3)_2$), 2.36–2.24 (m, 6H, H_{Ad}), 2.02 (m, 11H, H_{Ad}), 1.73 (m, 13H, H_{Ad}) ppm.

^{19}F NMR (376 MHz, CD_3CN): δ -58.7 ppm.

^{31}P{^{1}H} NMR (162 MHz, CD_3CN): δ 76.8 ppm.

ESI-MS(+): 814.17 (calc'd 814.25) *m/z* ($C_{35}H_{44}ClOF_3NPAu$).

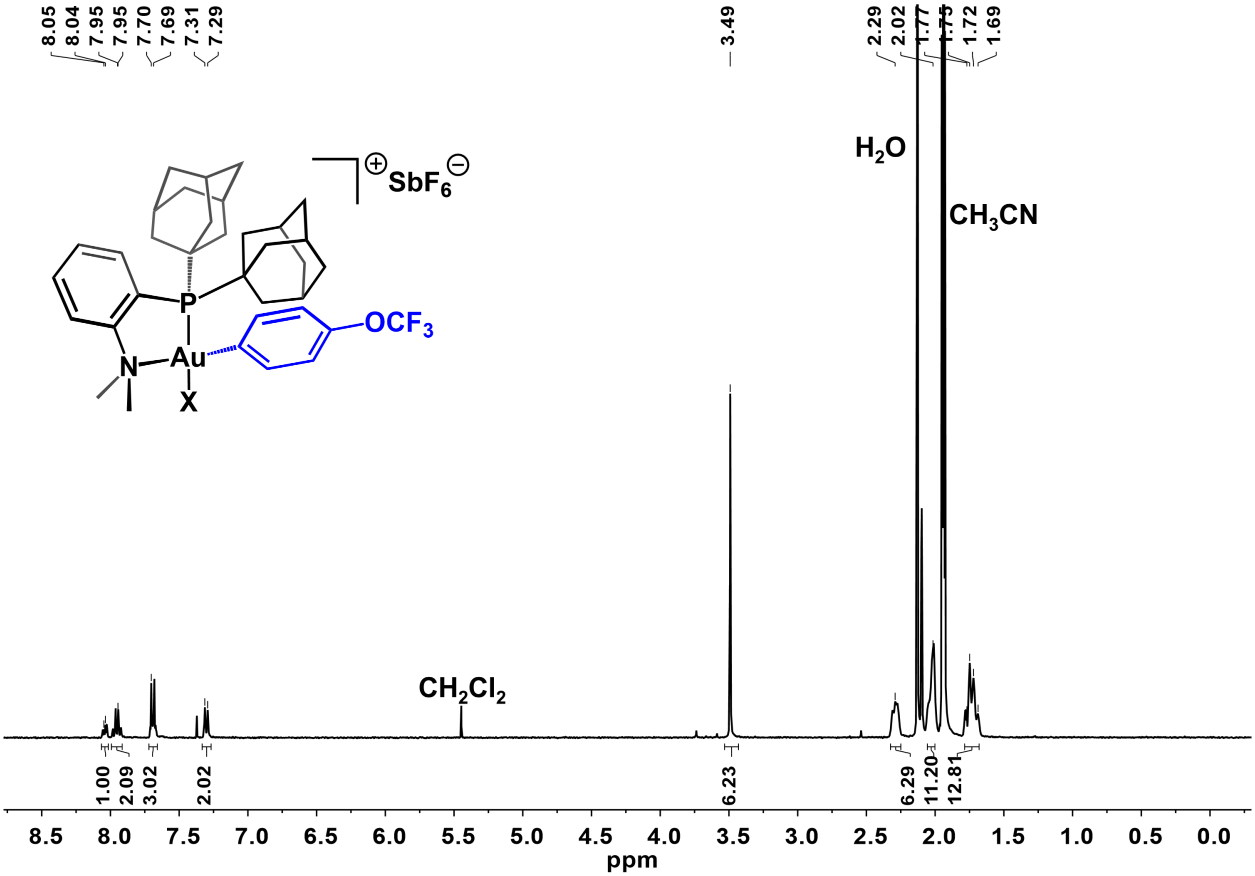


Figure S27. ^{1}H NMR spectrum of [**2g**][SbF_6] in CD_3CN at 298 K.

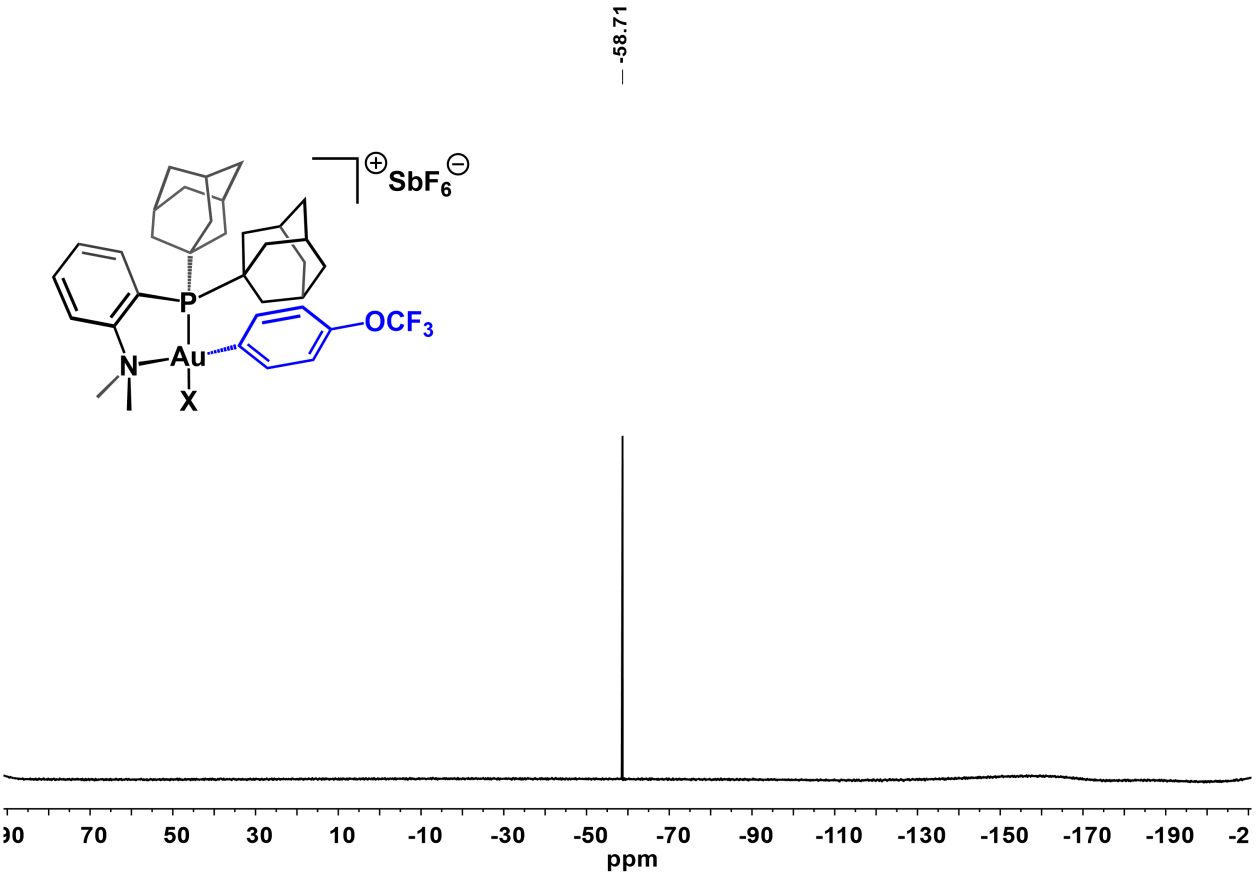


Figure S28. ^{19}F NMR spectrum of [**2g**][SbF$_6$] in CD$_3$CN at 298 K.

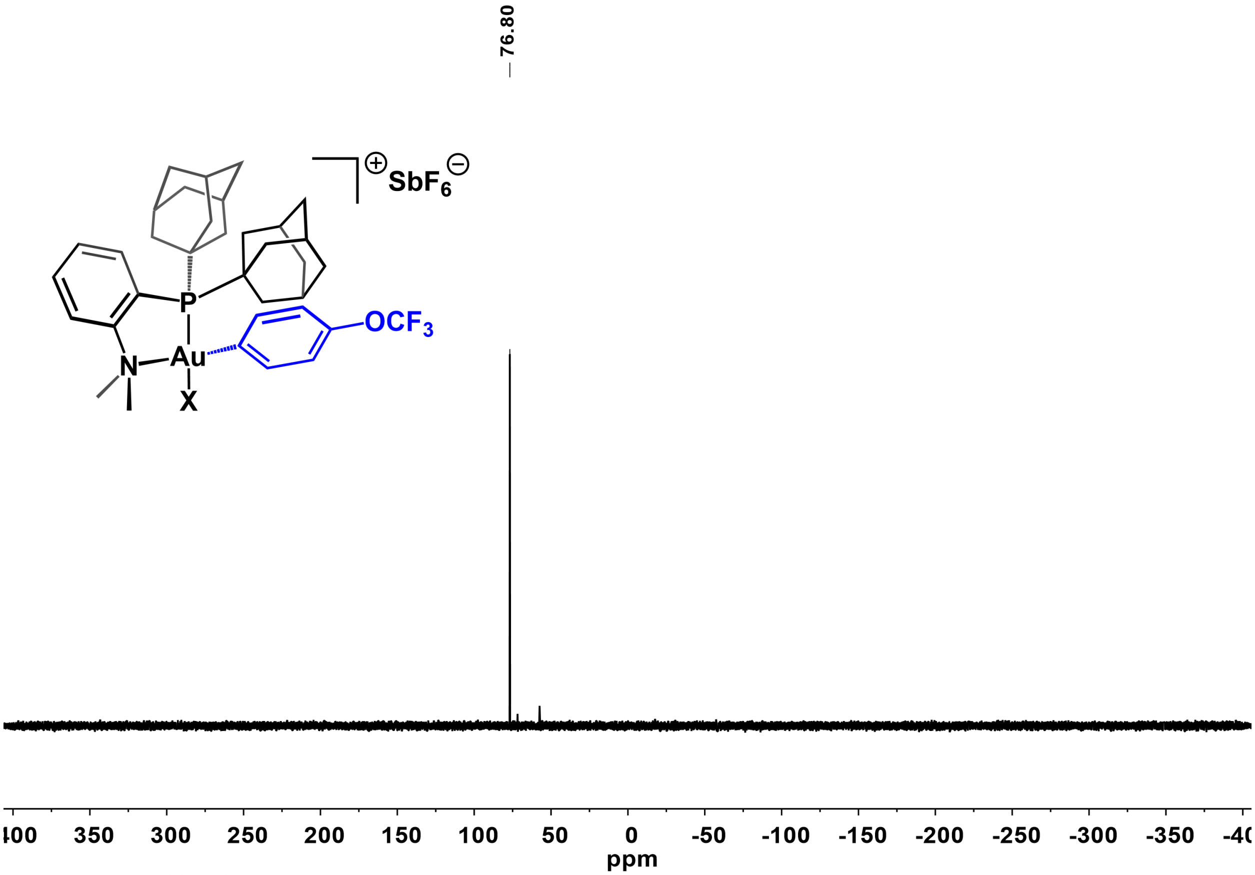


Figure S29. ^{31}P{^{1}H} NMR spectrum of [**2g**][SbF$_6$] in CD$_3$CN at 298 K.

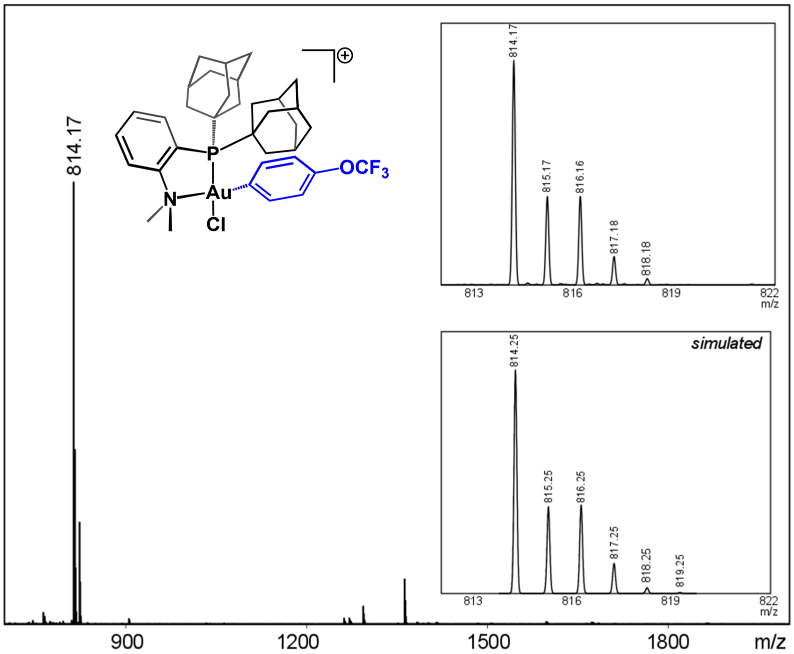
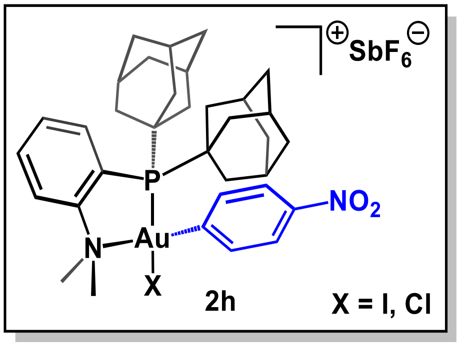


Figure S30. ESI-MS(+) of **2g**.



Following the general procedure, (Me-DalPhos)AuCl (30 mg, 0.046 mmol, 1.0 equiv), $AgSbF_6$ (16 mg, 0.046 mmol, 1.0 equiv) and 1-iodo-4-nitrobenzene (34 mg, 0.14 mmol, 3.0 equiv) were used. The [**2h**][SbF_6] salt was isolated as an orange crystalline solid in 75% yield (35 mg, 0.035 mmol). This complex has been previously reported.[3]

^{1}H NMR (400 MHz, CD_3CN): δ 8.16 (d, *J* = 9.0 Hz, 2H, H_{Ar}), 8.05 (m, 1H, H_{Ar}), 7.96 (m, 1H, H_{Ar}), 7.90 (d, *J* = 9.1 Hz, 2H, H_{Ar}), 7.70 (m, 1H, H_{Ar}), 3.52 (s, 6H, $N(CH_3)_2$), 2.41–2.22 (m, 6H, H_{Ad}), 2.07–1.99 (m, 12H, H_{Ad}), 1.74 (m, 12H, H_{Ad}) ppm.

^{31}P{^{1}H} NMR (162 MHz, CD_3CN): δ 79.9 ppm.

ESI-MS(+): 775.19 (calc'd 775.25) *m/z* ($C_{34}H_{44}ClN_2O_2PAu$).

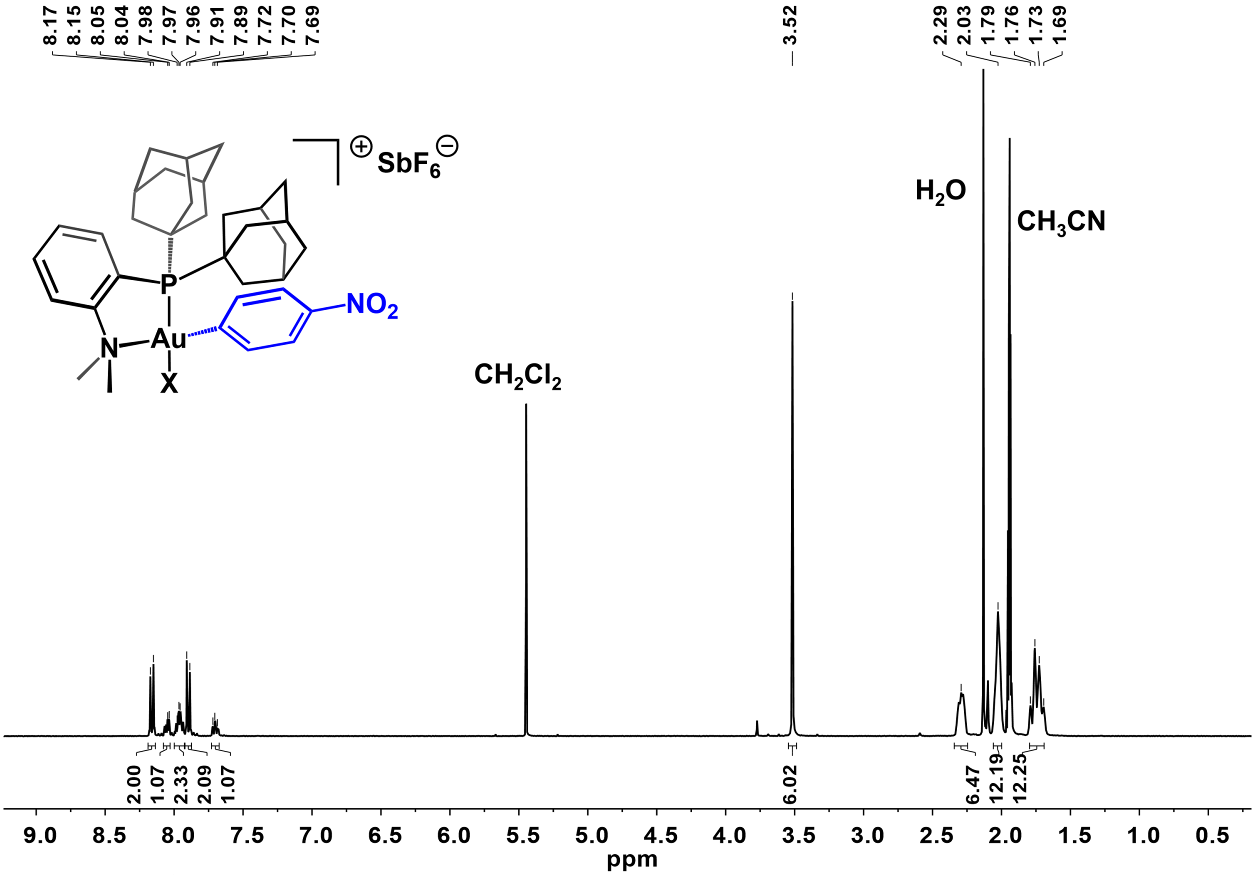


Figure S31. ^{1}H NMR spectrum of [**2h**][SbF_6] in CD_3CN at 298 K.

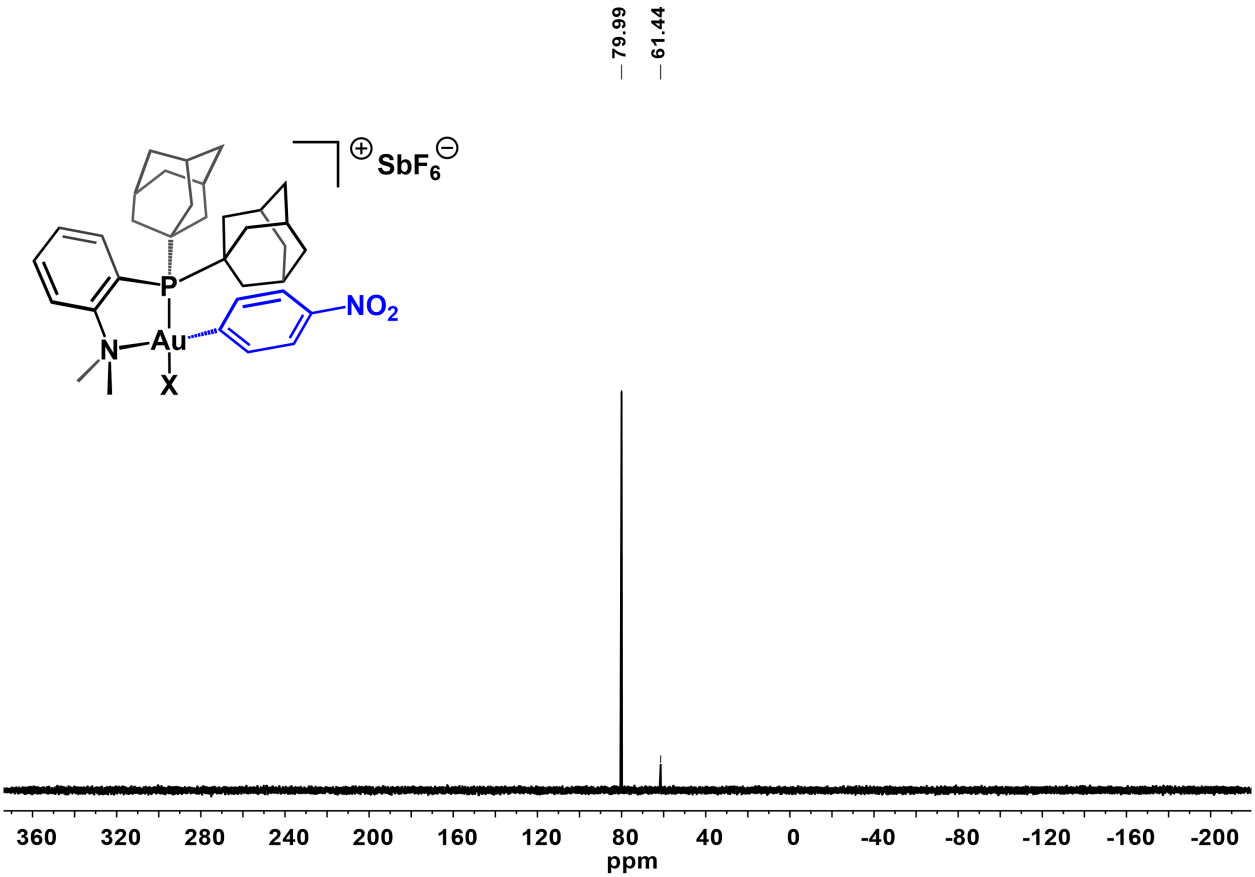


Figure S32. $^{31}P\{^1H\}$ NMR spectrum of [**2h**][SbF_6] in CD_3CN at 298 K.

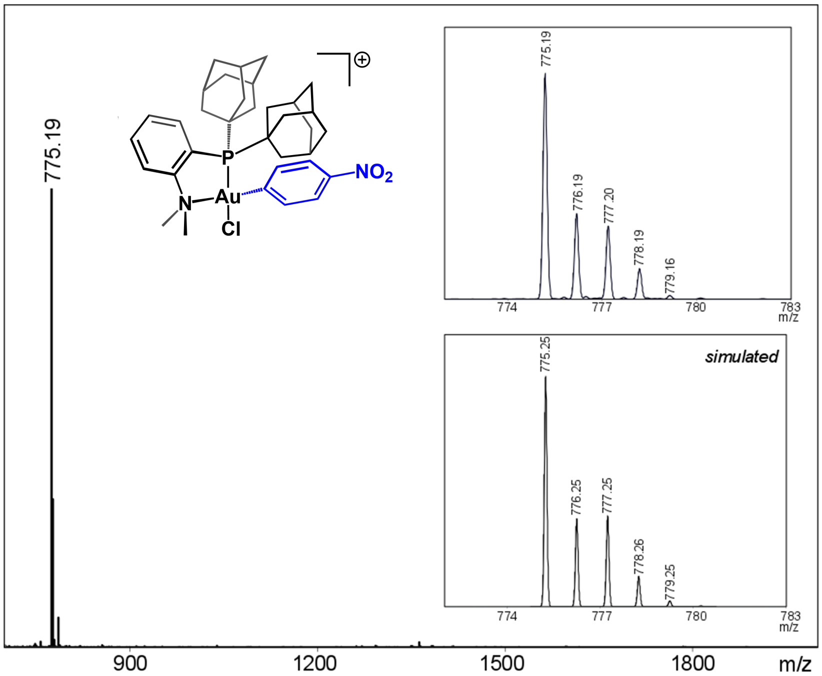
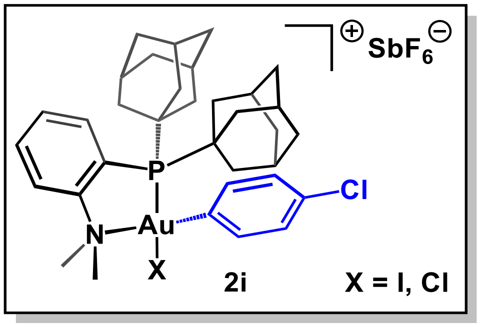


Figure S33. ESI-MS(+)of **2h**.



2i

Following the general procedure, (Me-DalPhos)AuCl (66 mg, 0.10 mmol, 1.0 equiv), $AgSbF_6$ (34 mg, 0.10 mmol, 1.0 equiv) and 1-chloro-4-iodobenzene (120 mg, 0.50 mmol, 5.0 equiv) were used. The [**2i**][SbF_6] salt was isolated as a yellow crystalline solid in 87% yield (87 mg, 0.087 mmol). A single crystal of suitable quality for an X-ray diffraction study was obtained using this procedure (see section V for crystallographic details).

^{1}H NMR (400 MHz, CD_3CN): δ 8.04 (dd, *J* = 8.2, 4.0 Hz, 1H, H_{Ar}), 8.00–7.91 (m, 2H, H_{Ar}), 7.73–7.65 (m, 1H, H_{Ar}), 7.58 (d, *J* = 8.7 Hz, 1H, H_{Ar}), 7.37 (d, *J* = 8.6 Hz, 1H, H_{Ar}), 3.48 (s, 6H, $N(CH_3)_2$), 2.29 (m, 6H, H_{Ad}), 2.02 (s, 11H, H_{Ad}), 1.74 (m, 13H, H_{Ad}) ppm.

^{31}P{^{1}H} NMR (162 MHz, CD_3CN): δ 77.6 ppm.

ESI-MS(+): 764.15 (calc'd 764.23) *m/z* ($C_{34}H_{44}Cl_2NPAu$).

Elem. Anal. (Calc'd) for $C_{34}H_{44}AuCl_2F_6NPSb$: C, 40.50 (40.76); H, 4.24 (4.43); N, 1.37 (1.40).

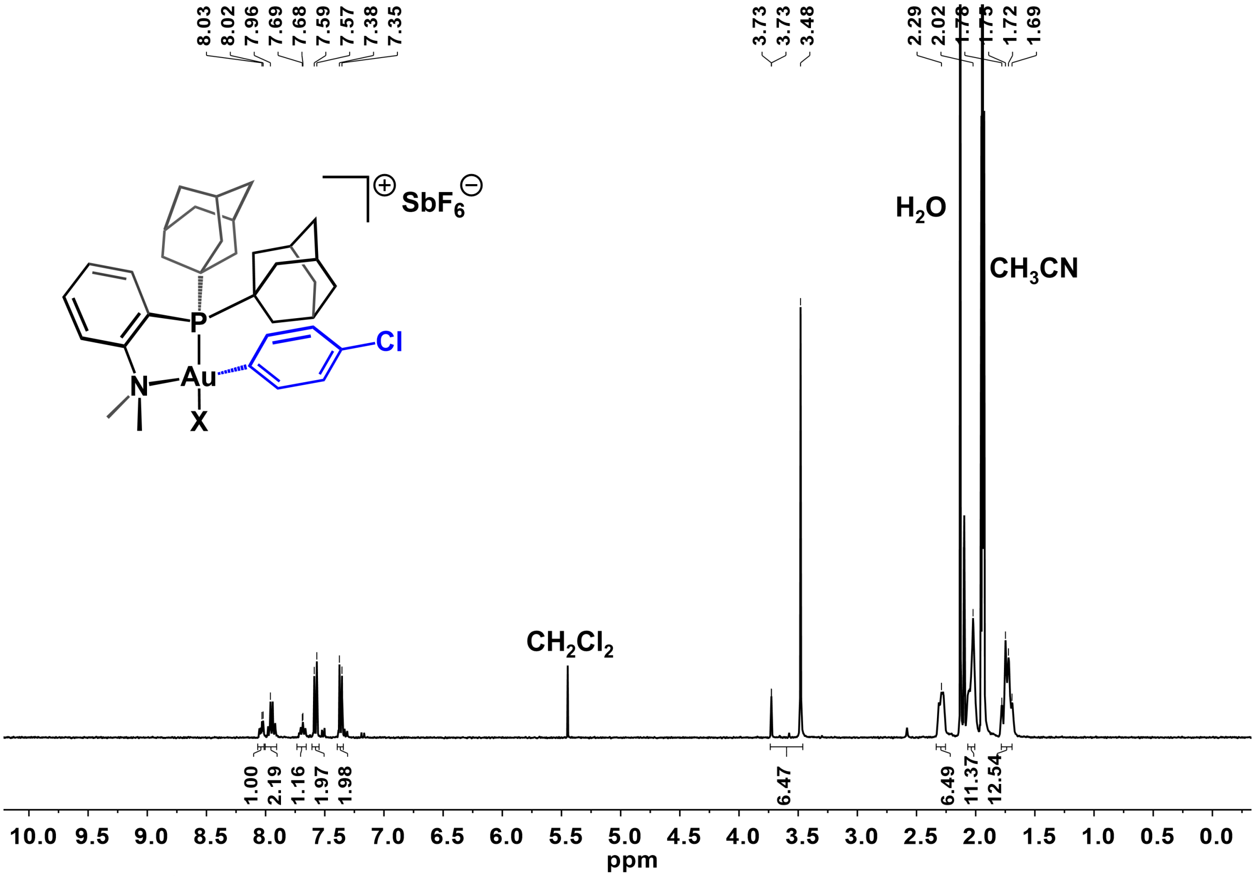


Figure S34. ^{1}H NMR spectrum of [**2i**][SbF_6] in CD_3CN at 298 K.

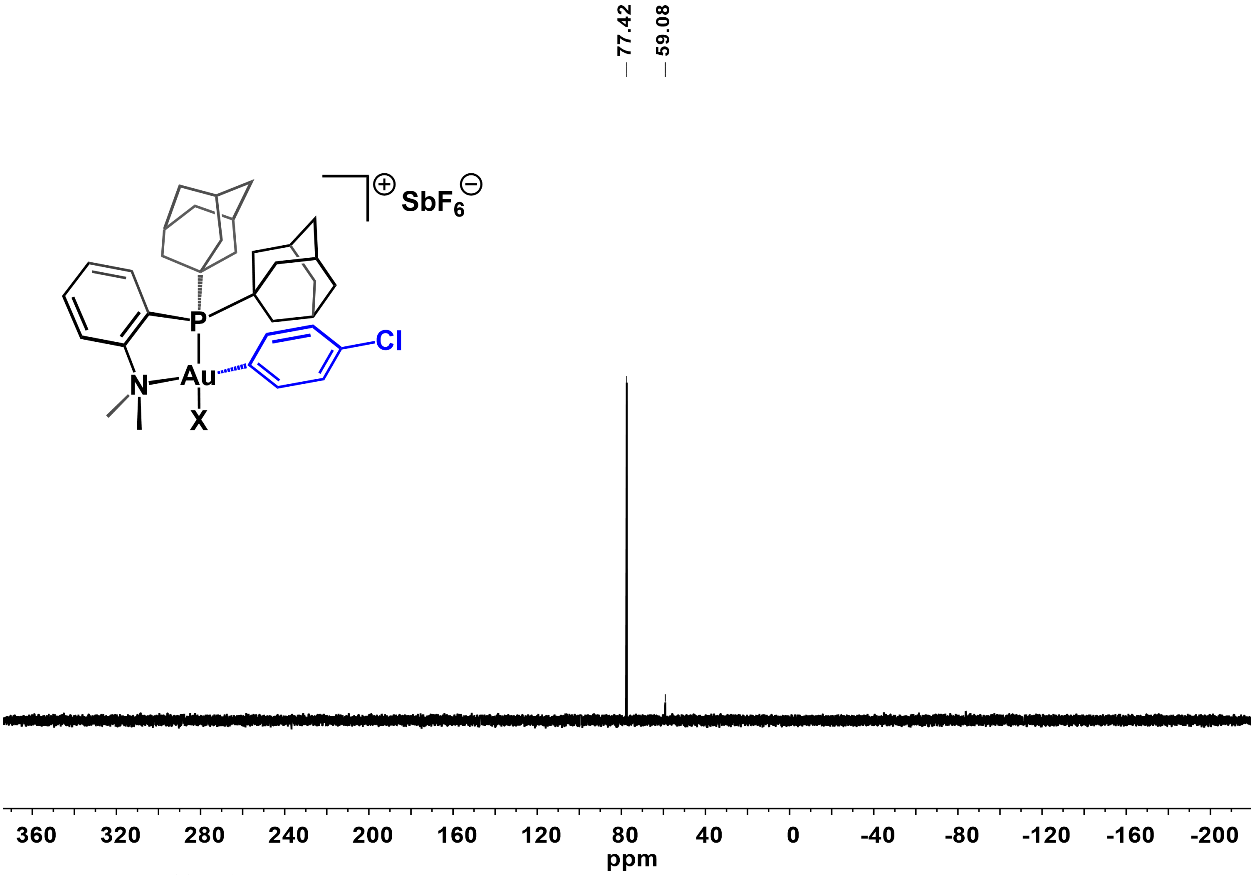


Figure S35. $^{31}P\{^{1}H\}$ NMR spectrum of [**2i**][SbF_6] in CD_3CN at 298 K. The signal at 59.0 ppm corresponds to the starting (Me-DalPhos)AuCl compound.

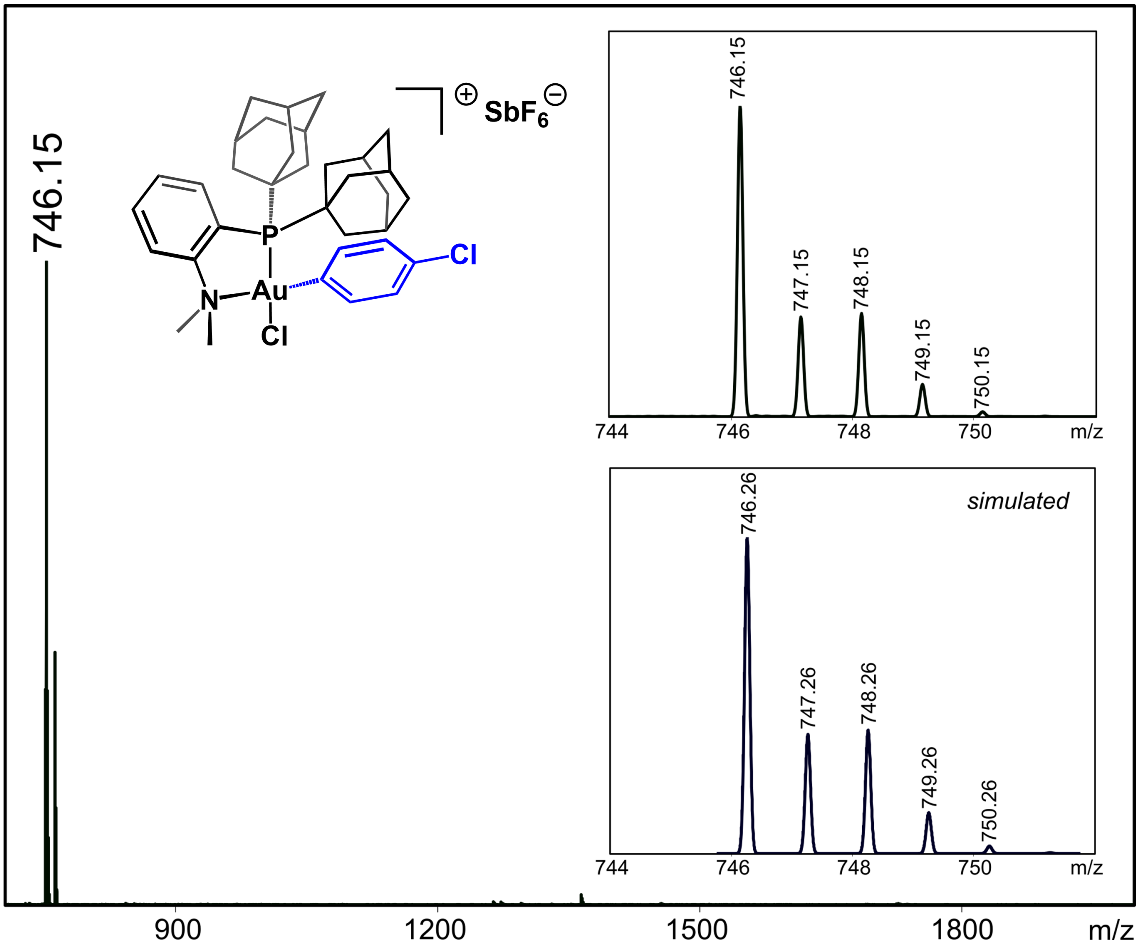
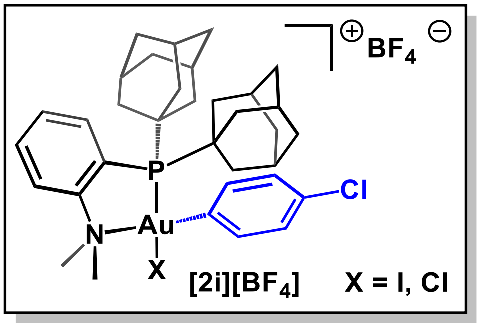


Figure S36. ESI-MS(+) of **2i**.



[2i][BF$_4$]

In the fume hood, a solution of $AgBF_4$ (9 mg, 0.05 mmol, 1 equiv) in DCM (2 mL) was prepared under protection from light, and then cooled to -20 °C. A DCM solution (2 mL) containing 4-chloroiodobenzene (55 mg, 0.23 mmol, 5.0 equiv) and (Me-DalPhos)AuCl (30 mg, 0.046 mmol, 1.0 equiv) reagents was prepared and also cooled to -20 °C. While both solutions were cold, the colorless 4-chloroliodobenzene and (Me-DalPhos)AuCl solution was added in one portion to the solution of $AgBF_4$, and the reaction mixture was sonicated for 2 min, during which time the solution became yellow concomitant with the precipitation of pale yellow precipitate. The resulting suspension was filtered through a pad of Celite. Slow evaporation of solvent from the yellow filtrate over the course of 48 h at 25 °C resulted in saturation of the solution and the formation of yellow crystals. The supernatant was removed and the crystals were washed with C_6H_6 (2 x 3 mL), followed by *n*-pentane (2 × 3 mL), and then dried under reduced pressure to afford [**2i**][BF_4] as a yellow crystalline solid in 61% yield (26 mg, 0.031 mmol).

^{1}H NMR (400 MHz, CD_3CN): δ 8.03 (m, 1H, H_{Ar}), 7.95 (m, 2H, H_{Ar}), 7.73–7.68 (m, 1H, H_{Ar}), 7.58 (d, 2H, *J* = 8.7 Hz, H_{Ar}), 7.37 (d, 2H, *J* = 8.7 Hz, H_{Ar}), 3.48 (s, 6H, $N(CH_3)_2$), 2.29 (s, 6H, H_{Ad}), 2.10 (s, 6H, H_{Ad}), 2.03 (s, 6H, H_{Ad}), 1.75 (s, 12H, H_{Ad}) ppm.

^{31}P{^{1}H} NMR (162 MHz, CD_3CN): δ 77.4 ppm.

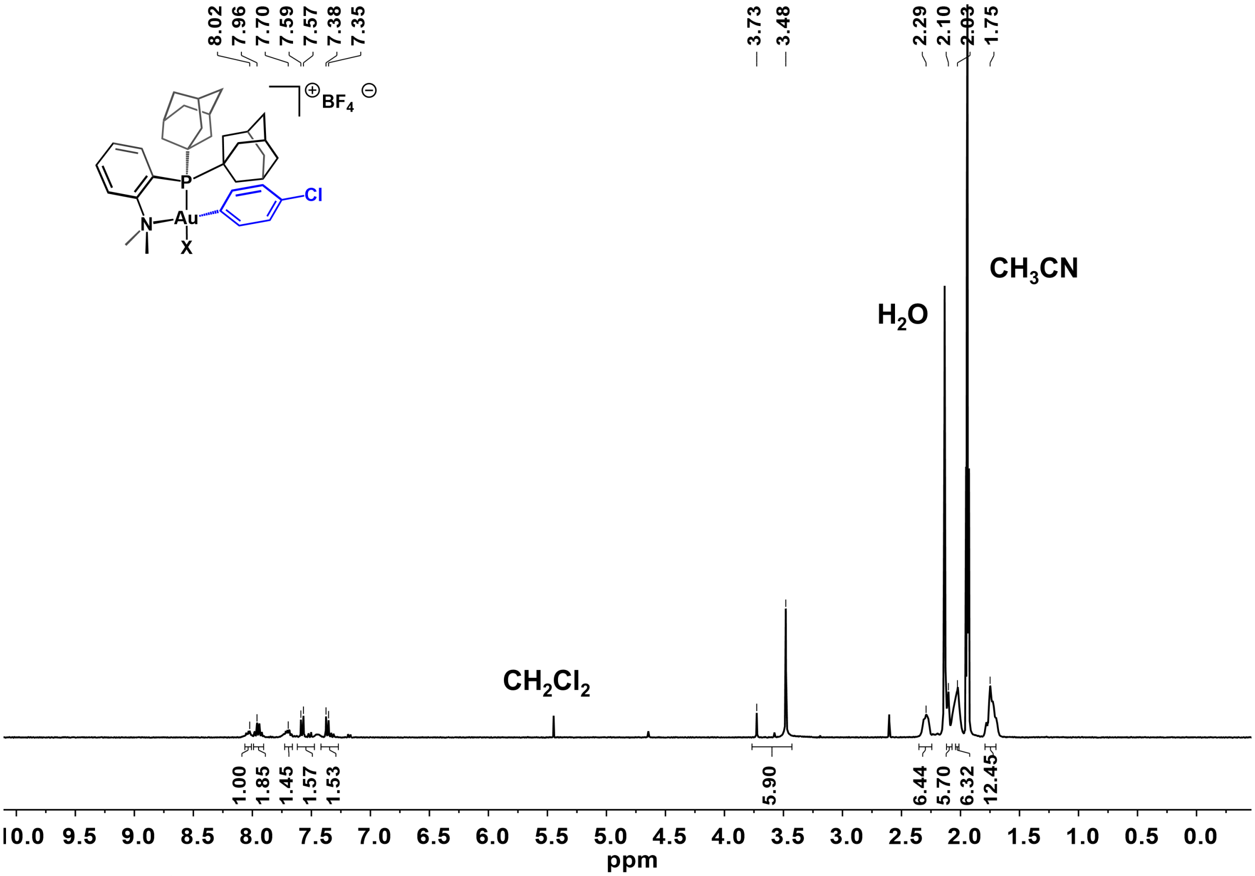


Figure S37. ^{1}H NMR spectrum of [**2i**][BF$_4$] in CD$_3$CN at 298 K.

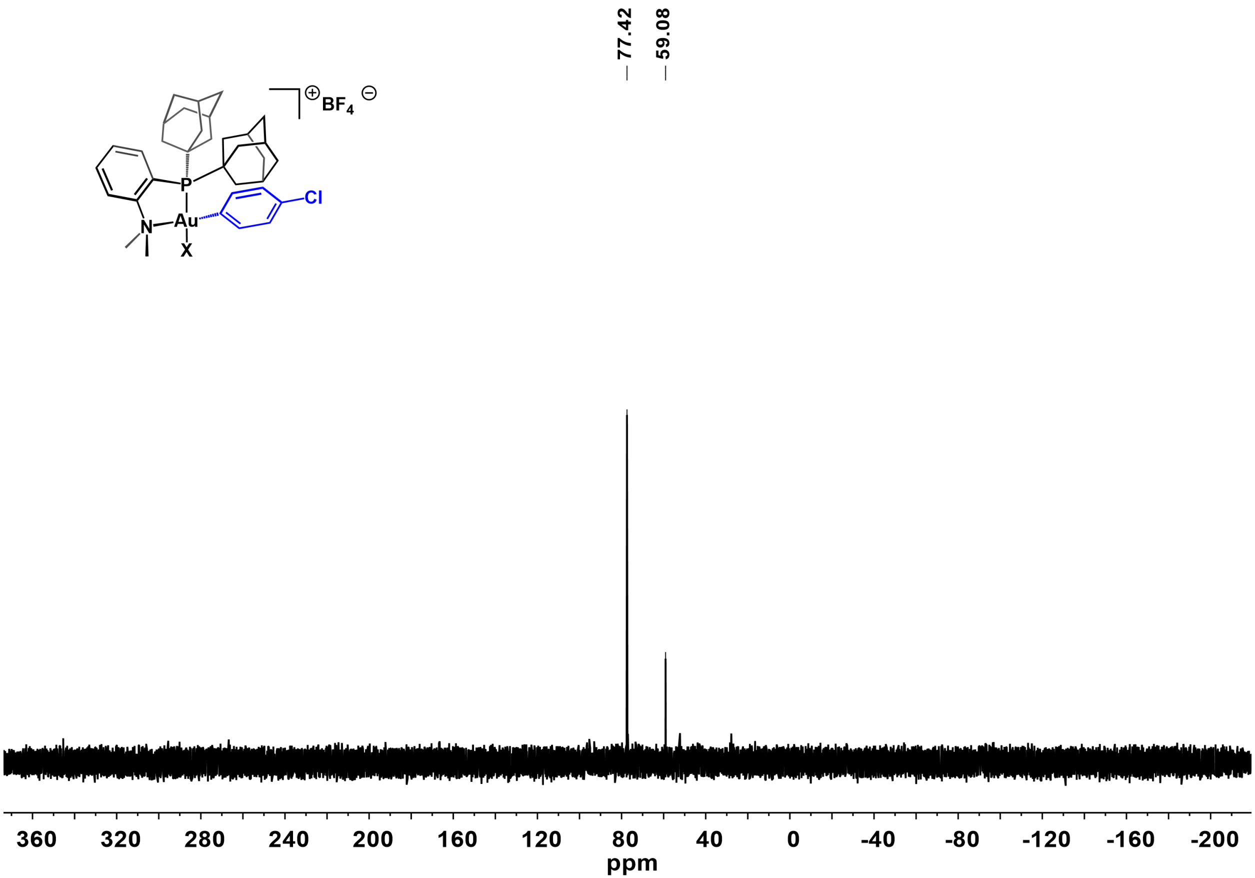
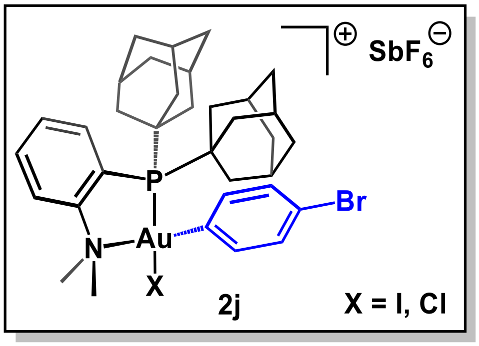


Figure S38. $^{31}P\{^1H\}$ NMR spectrum of [**2i**][BF$_4$] in CD$_3$CN at 298 K. The signal at 59.0 ppm corresponds to the starting (Me-DalPhos)AuCl compound.



2j X = I, Cl

Following the general procedure, (Me-DalPhos)AuCl (30 mg, 0.046 mmol, 1.0 equiv), $AgSbF_6$ (16 mg, 0.046 mmol, 1.0 equiv) and 1-bromo-4-iodobenzene (65 mg, 0.23 mmol, 5.0 equiv) were used. The [**2j**][SbF_6] salt was isolated as a yellow crystalline solid in 82% yield (39 mg, 0.038 mmol). A single crystal of suitable quality for an X-ray diffraction study was obtained using this workup (See section V for crystallographic details). Elem. Anal. (Calc'd) for $C_{34}H_{44}AuBrClF_6NPSb$: C, 38.56 (39.03); H, 4.03 (4.24); N, 1.29 (1.34). The low value observed for carbon is likely due to crystallization of **2j** as a mixture of [(Me-DalPhos)Au(*p*-Br-C_6H_4)Cl]$^+$ and [(Me-DalPhos)Au(*p*-Br-C_6H_4)I]$^+$ species as confirmed by X-ray structural analysis of a single-crystal obtained from the described procedure. The X-ray structural analysis indicates 77% Cl and 23% I occupancy.

^{1}H NMR (400 MHz, CD_3CN): δ 8.02 (m, 1H, H_{Ar}), 7.99–7.88 (m, 2H, H_{Ar}), 7.72–7.62 (m, 1H, H_{Ar}), 7.49 (m, 4H, H_{Ar}), 3.46 (s, 6H, N(CH_3)$_2$), 2.27 (m, 6H, H_{Ad}), 2.04 (m, 12H, H_{Ad}), 1.72 (m, 12H, H_{Ad}) ppm.

^{31}P{^{1}H} NMR (162 MHz, CD_3CN): δ 77.6 ppm.

ESI-MS(+): 808.18 (calc'd 808.17) *m/z* ($C_{34}H_{44}ClBrNPAu$).

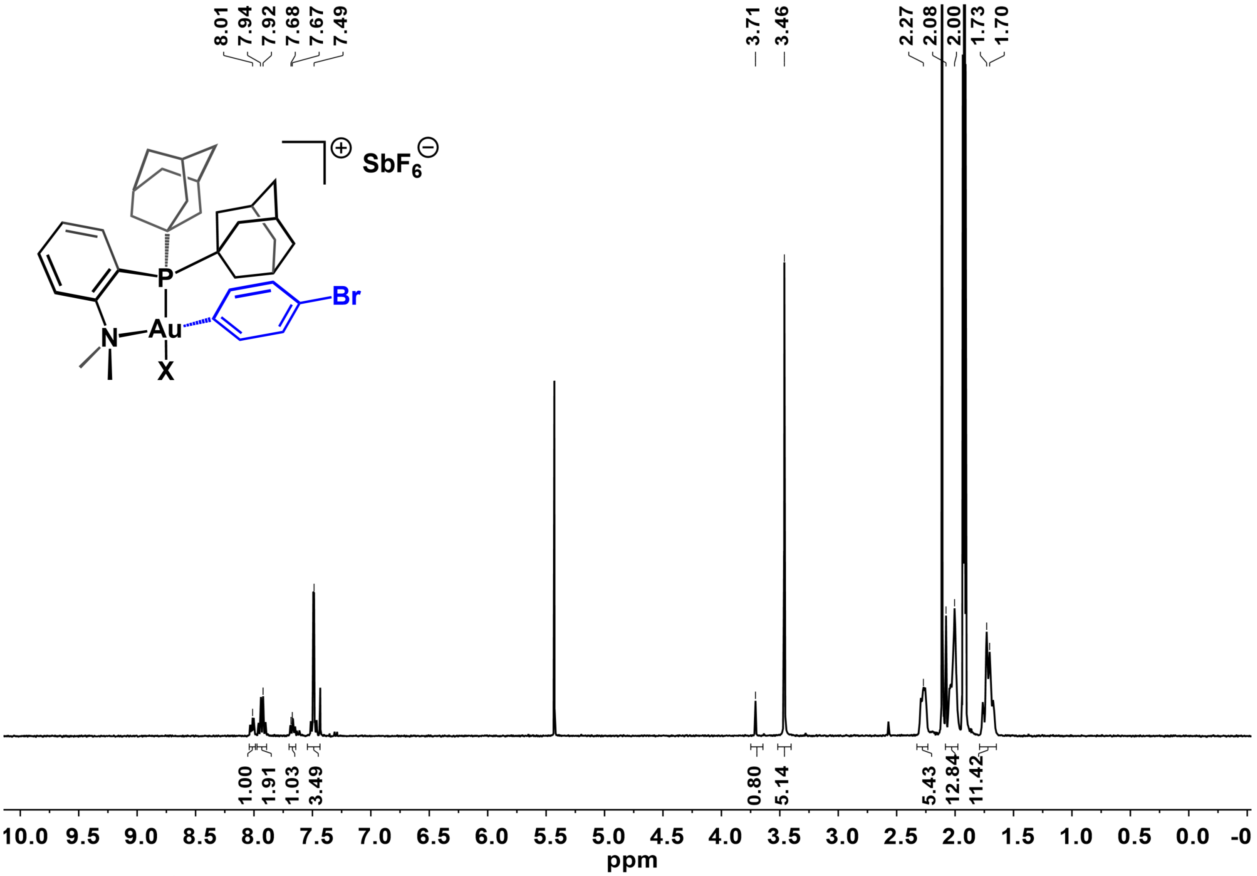


Figure S39. ^{1}H NMR spectrum of [**2j**][SbF$_6$] in CD$_3$CN at 298 K.

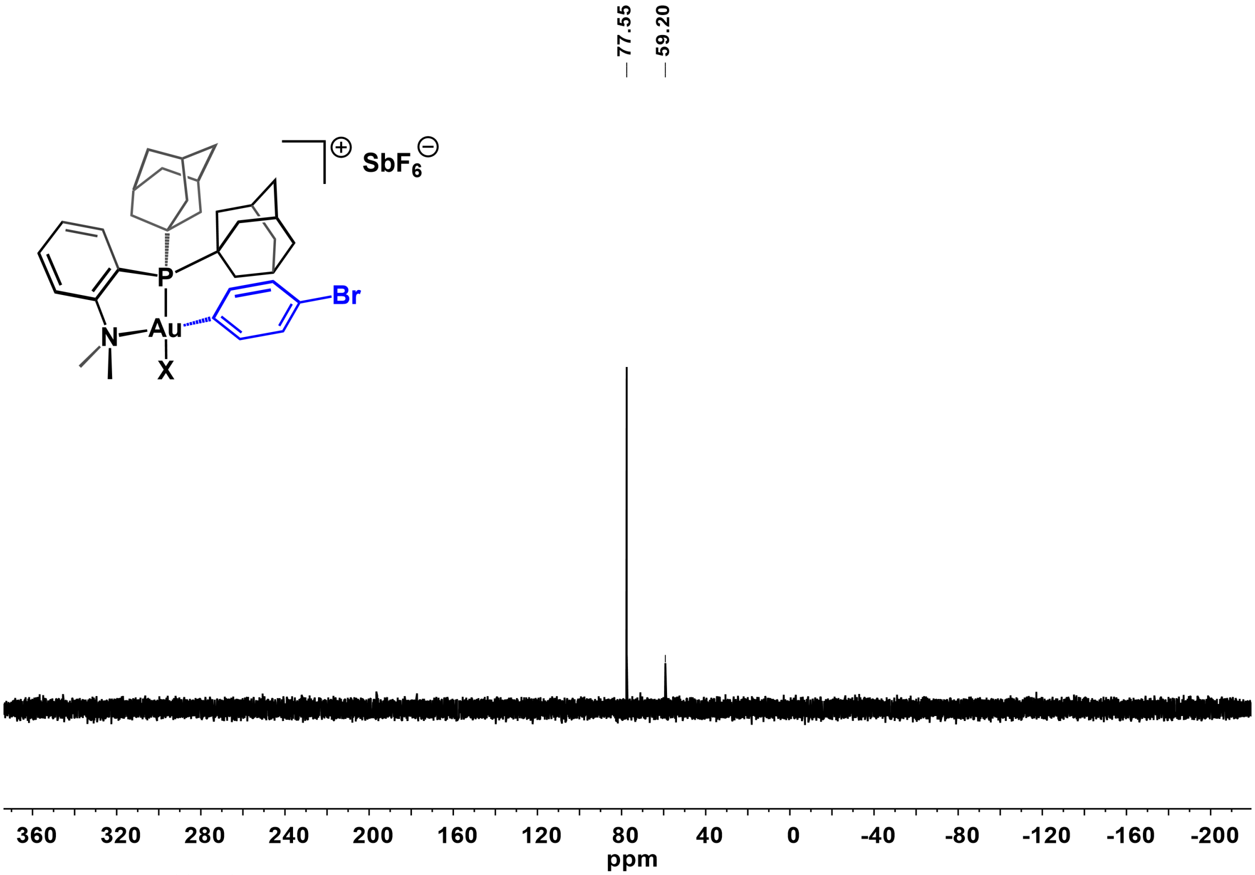


Figure S40. $^{31}P\{^{1}H\}$ NMR spectrum of [**2j**][SbF$_6$] in CD$_3$CN at 298 K. The signal at 59.2 ppm corresponds to the starting (Me-DalPhos)AuCl compound.

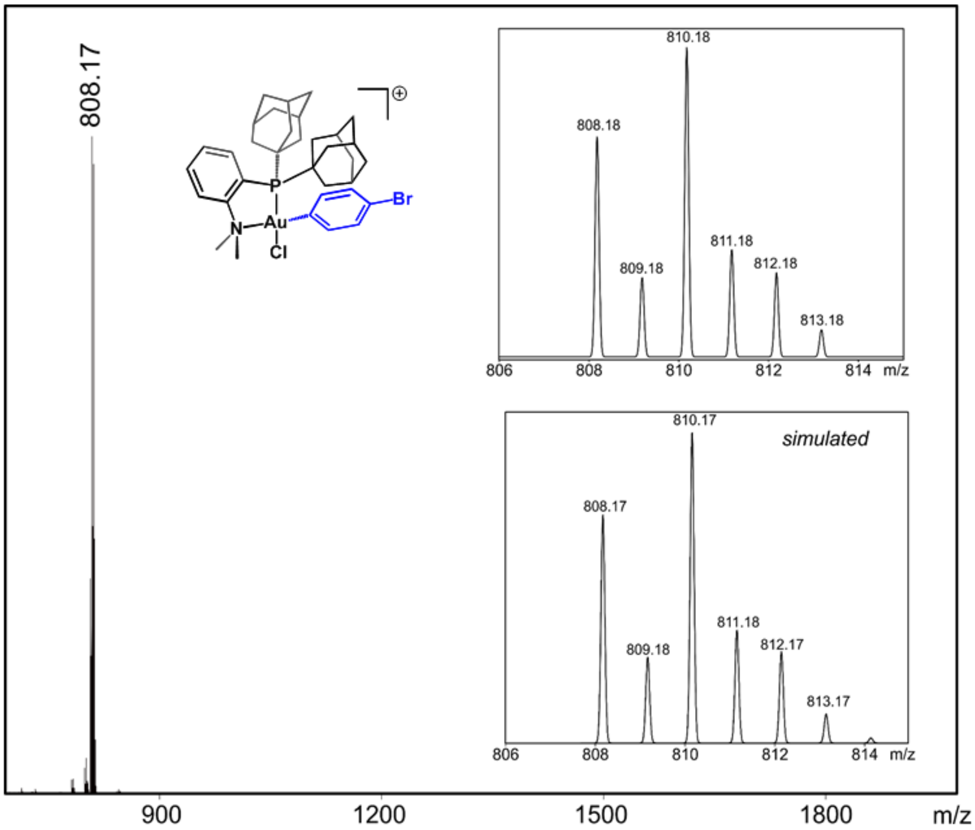
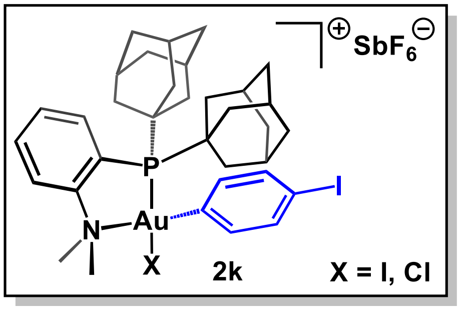


Figure S41. ESI-MS(+) of **2j**.



2k

Following the general procedure, (Me-DalPhos)AuCl (30 mg, 0.046 mmol, 1.0 equiv), $AgSbF_6$ (16 mg, 0.046 mmol, 1.0 equiv) and 1,4-diiodobenzene (76 mg, 0.23 mmol, 5.0 equiv) were used. The [**2k**][SbF_6] salt was isolated as a yellow crystalline solid in 73% yield (37 mg, 0.034 mmol).

^{1}H NMR (400 MHz, CD_3CN): δ 8.03 (dd, *J* = 8.4, 4.0 Hz, 1H, H_{Ar}), 7.99–7.90 (m, 2H, H_{Ar}), 7.72–7.67 (m, 1H, H_{Ar}), 7.66 (d, *J* = 8.4 Hz, 2H, H_{Ar}), 7.38 (d, *J* = 8.5 Hz, 2H, H_{Ar}), 3.47 (s, 6H, $N(CH_3)_2$), 2.36–2.22 (m, 6H, H_{Ad}), 2.04 (d, *J* = 16.7 Hz, 13H, H_{Ad}), 1.73 (d, *J* = 10.4 Hz, 11H, H_{Ad}) ppm.

$^{31}P\{^1H\}$ NMR (162 MHz, CD_3CN): δ 77.6 ppm.

ESI-MS(+): 856.08 (calc'd 856.16) *m/z* ($C_{34}H_{44}ClINPAu$).

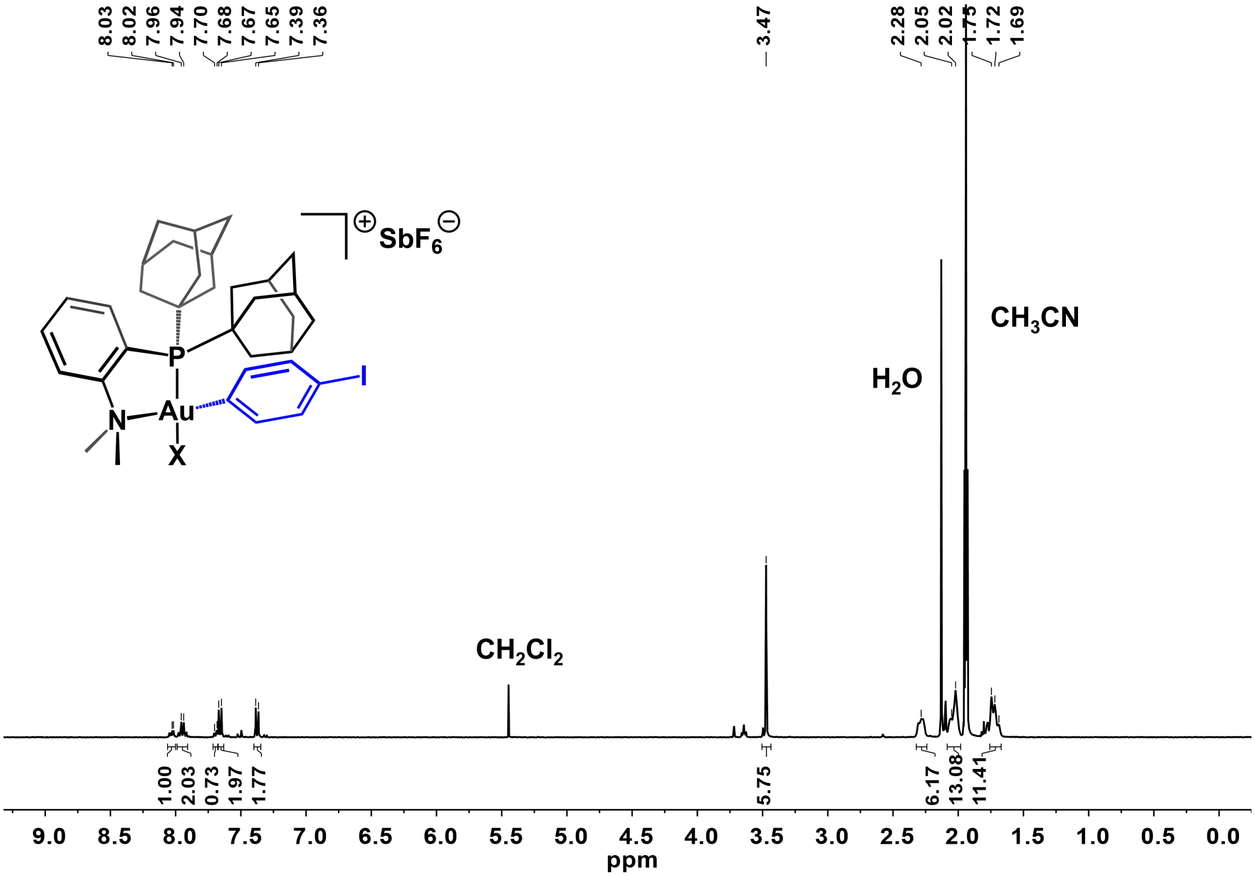


Figure S42. ^{1}H NMR spectrum of [**2k**][SbF_6] in CD_3CN at 298 K.

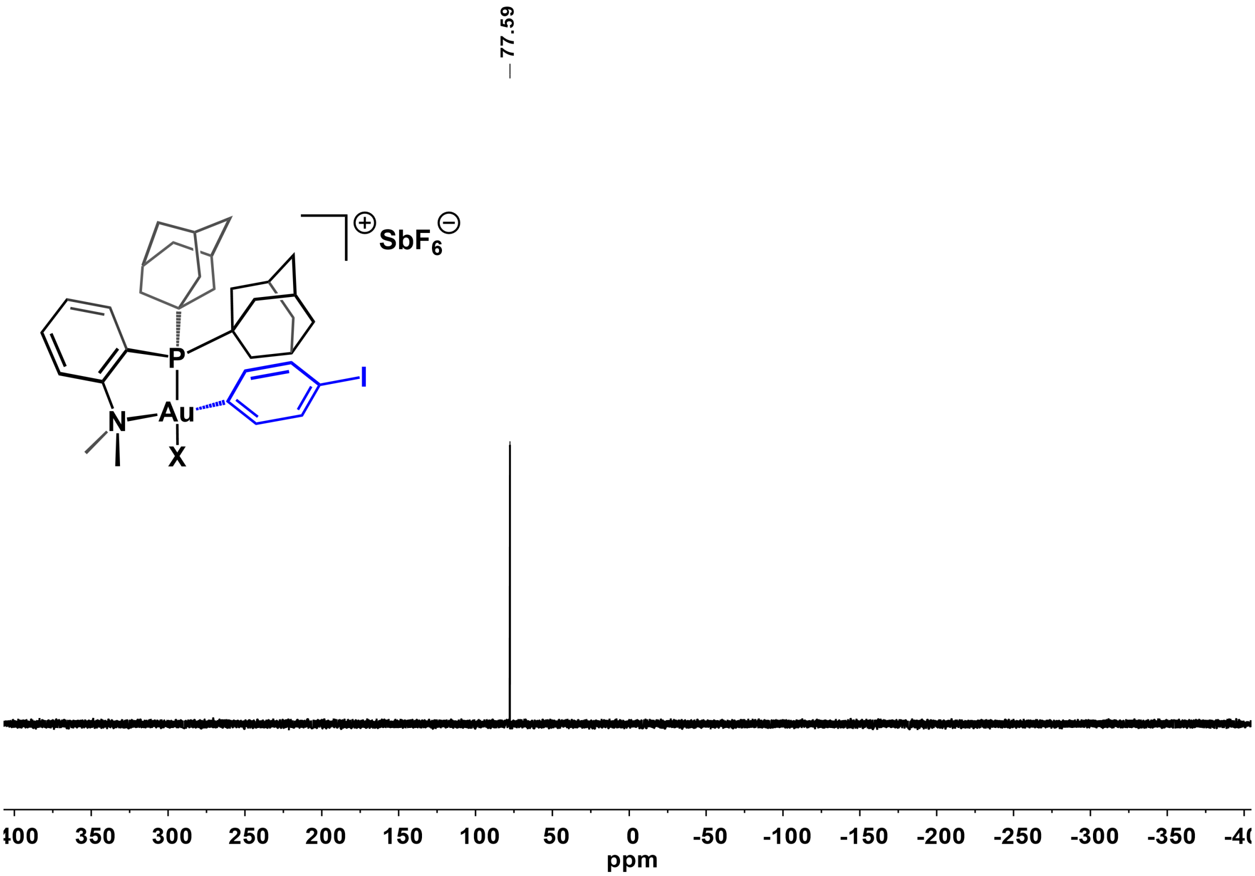


Figure S43. $^{31}P\{^1H\}$ NMR spectrum of [**2k**][SbF_6] in CD_3CN at 298 K.

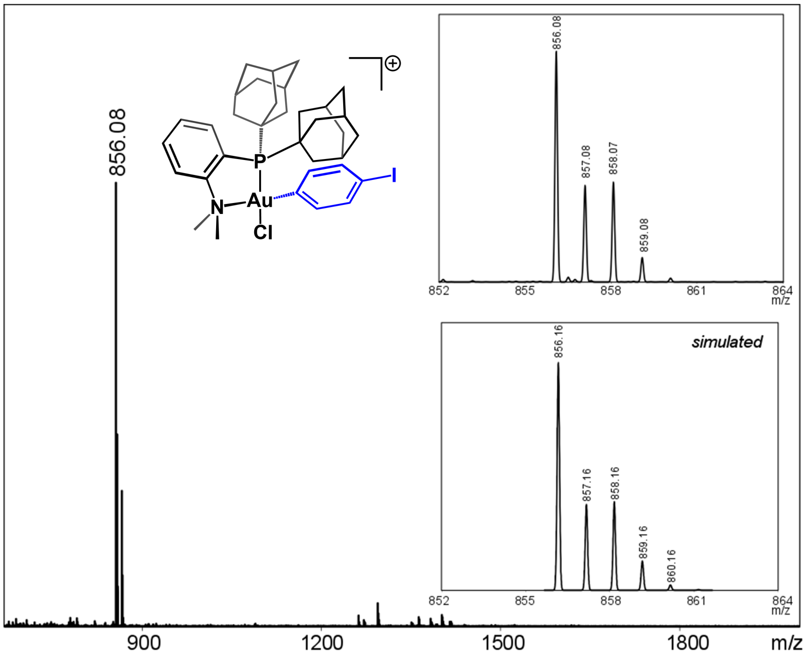
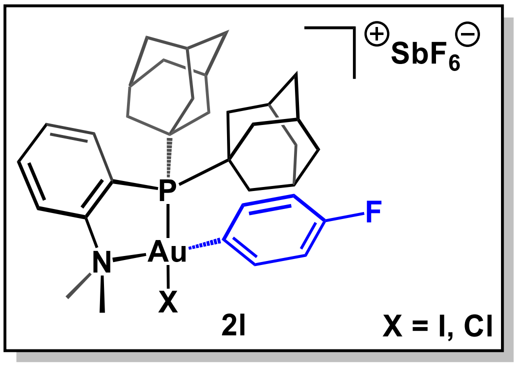


Figure S44. ESI-MS(+) of **2k**.



Following the general procedure, (Me-DalPhos)AuCl (30 mg, 0.046 mmol, 1.0 equiv), $AgSbF_6$ (16 mg, 0.046 mmol, 1.0 equiv) and 4-fluoroiodobenzene (16 µL, 0.14 mmol, 3.0 equiv) were used. The [**2l**][SbF_6] salt was isolated as a yellow crystalline solid in 74% yield (34 mg, 0.034 mmol). The spectroscopic features of the isolated material matched those reported in the literature for this salt.[5]

$^{31}P\{^{1}H\}$ NMR (162 MHz, CH_2Cl_2): δ 76.2 ppm.

ESI-MS(+): 748.25 (calc'd 748.20) *m/z* ($C_{34}H_{44}ClN_2PFAu$).

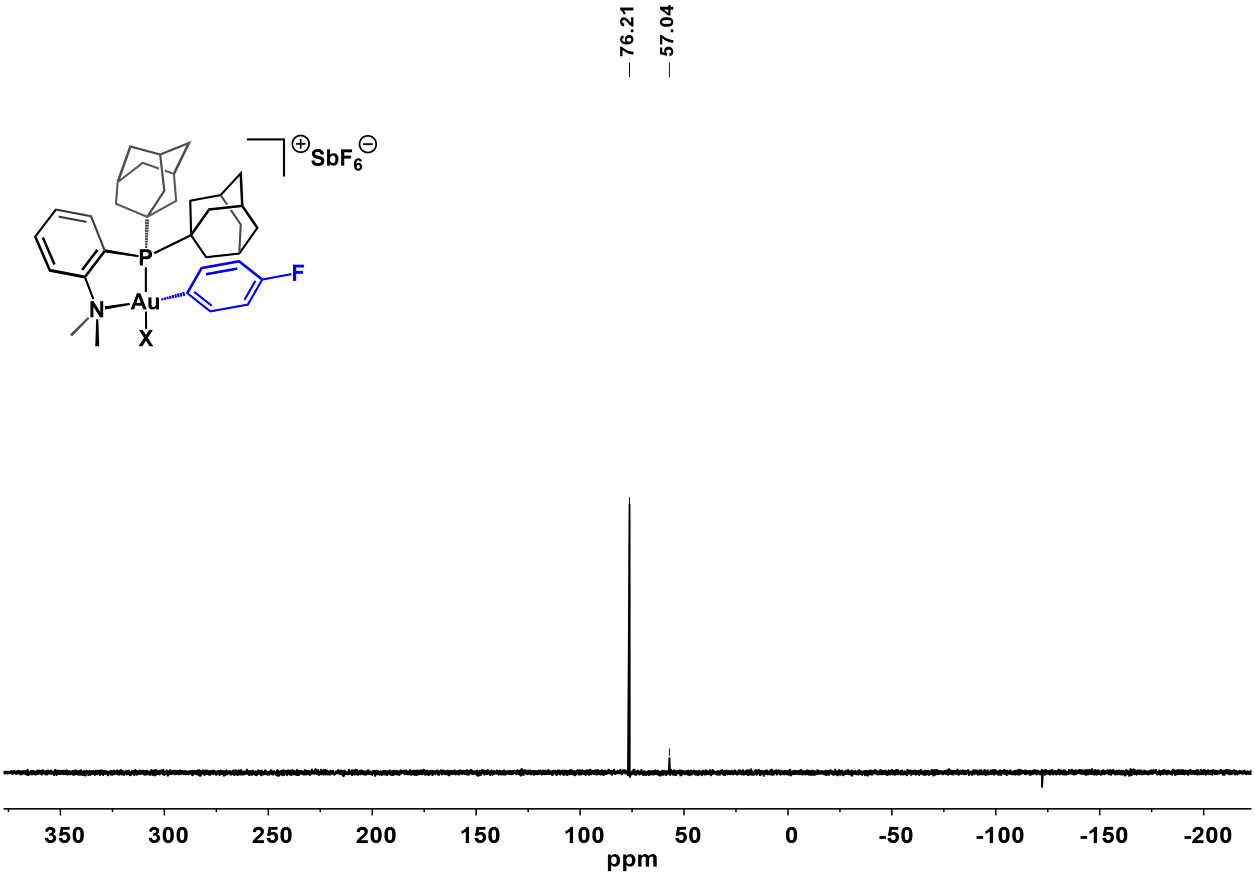


Figure S45. $^{31}P\{^{1}H\}$ NMR spectrum of [**2l**][SbF_6] in CH_2Cl_2 at 298 K.

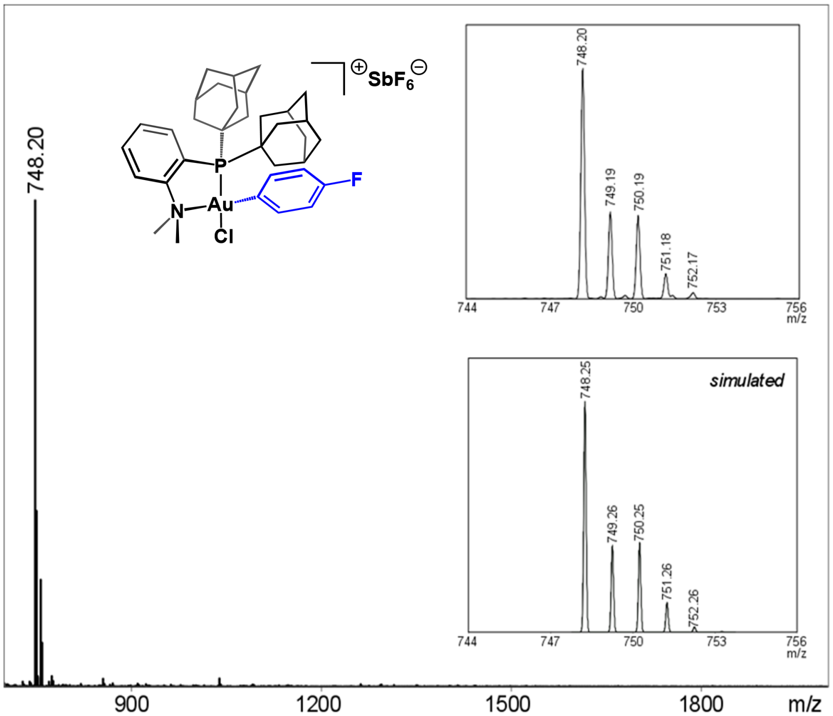
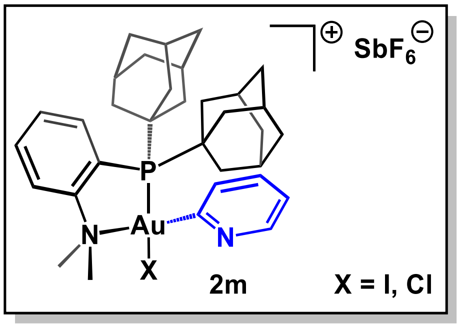


Figure S46. ESI-MS(+) of **2l**.



2m

In the fume hood, $AgSbF_6$ (9 mg, 0.03 mmol, 1 equiv) was dissolved in DCM (2 mL) under protection from light, and the colorless solution was cooled to -20 °C. A DCM solution (2 mL) containing 2-iodopyridine (20 µL, 0.17 mmol, 6.0 equiv) and (Me-DalPhos)AuCl (18 mg, 0.028 mmol, 1.0 equiv) reagents was prepared and also cooled to -20 °C. While both solutions were cold, the pale yellow 2-iodopyridine and (Me-DalPhos)AuCl solution was added in one portion to the solution of $AgSbF_6$. The solution was allowed to stand at 25 °C for 24 h, during which time pale yellow solids precipitated out of solution. The reaction mixture was filtered through a pad of Celite, and the resulting pale-yellow filtrate was dried under reduced pressure. The pale-yellow residue was washed with C_6H_6 (2 x 3 mL), followed by *n*-pentane (2 x 3 mL), and then dried under reduced pressure to afford [**2m**][SbF_6] as a pale yellow powder in 77% yield (22 mg, 0.023 mmol).

^{1}H NMR (400 MHz, CD_3CN): δ 8.50–8.46 (m, 1H, H_{Ar}), 8.02 (m, 1H, H_{Ar}), 8.00–7.88 (m, 3H, H_{Ar}), 7.74–7.55 (m, 3H, H_{Ar}), 7.22 (m, 1H, H_{Ar}), 3.42 (s, 6H, $N(CH_3)_2$), 2.36 (m, 6H, H_{Ad}), 2.00 (m, 12H, H_{Ad}), 1.84–1.64 (m, 12H, H_{Ad}) ppm.

^{31}P{^{1}H} NMR (162 MHz, CD_3CN): δ 70.4 ppm.

ESI-MS(+): 731.25 (calc'd 731.26) *m/z* ($C_{33}H_{44}ClN_2PAu$).

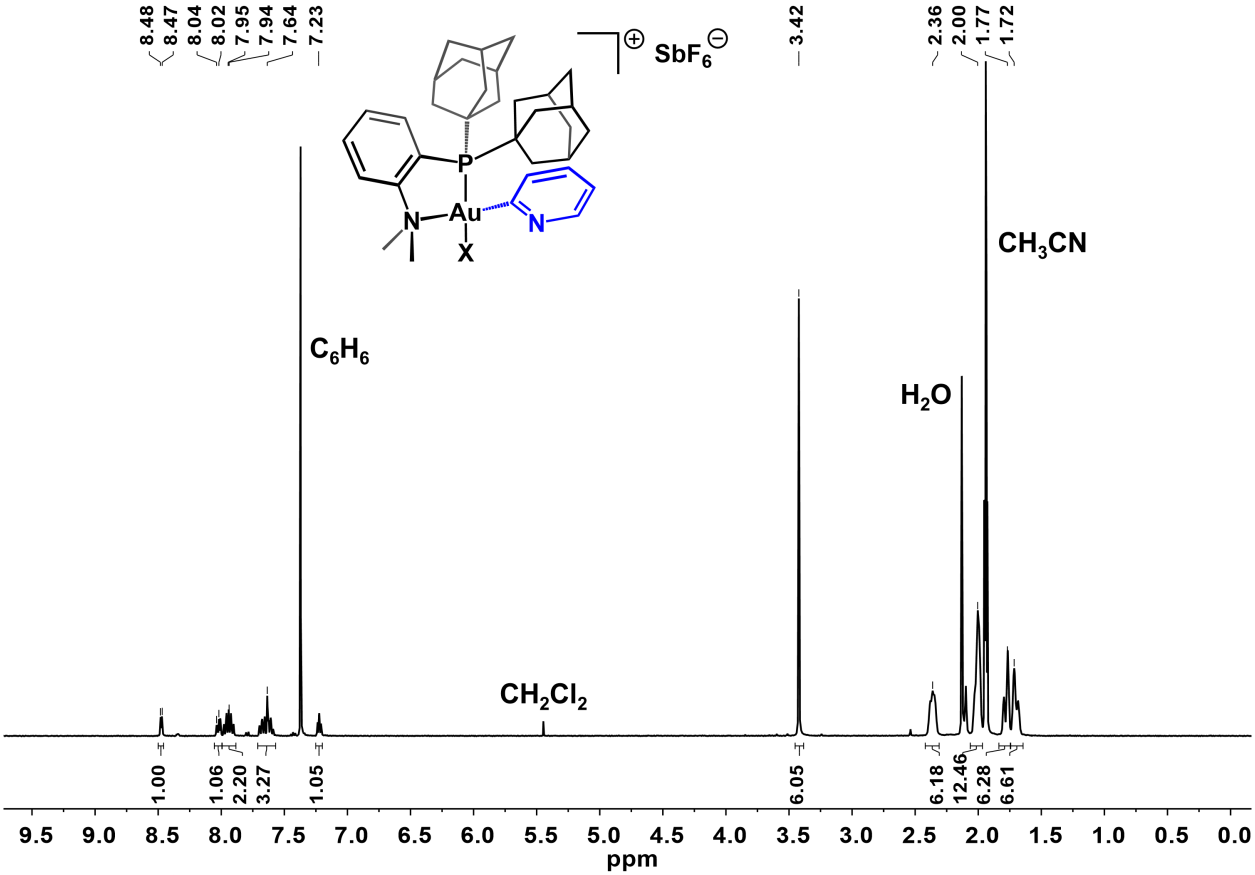


Figure S47. ^{1}H NMR spectrum of [**2m**][SbF_6] in CD_3CN at 298 K.

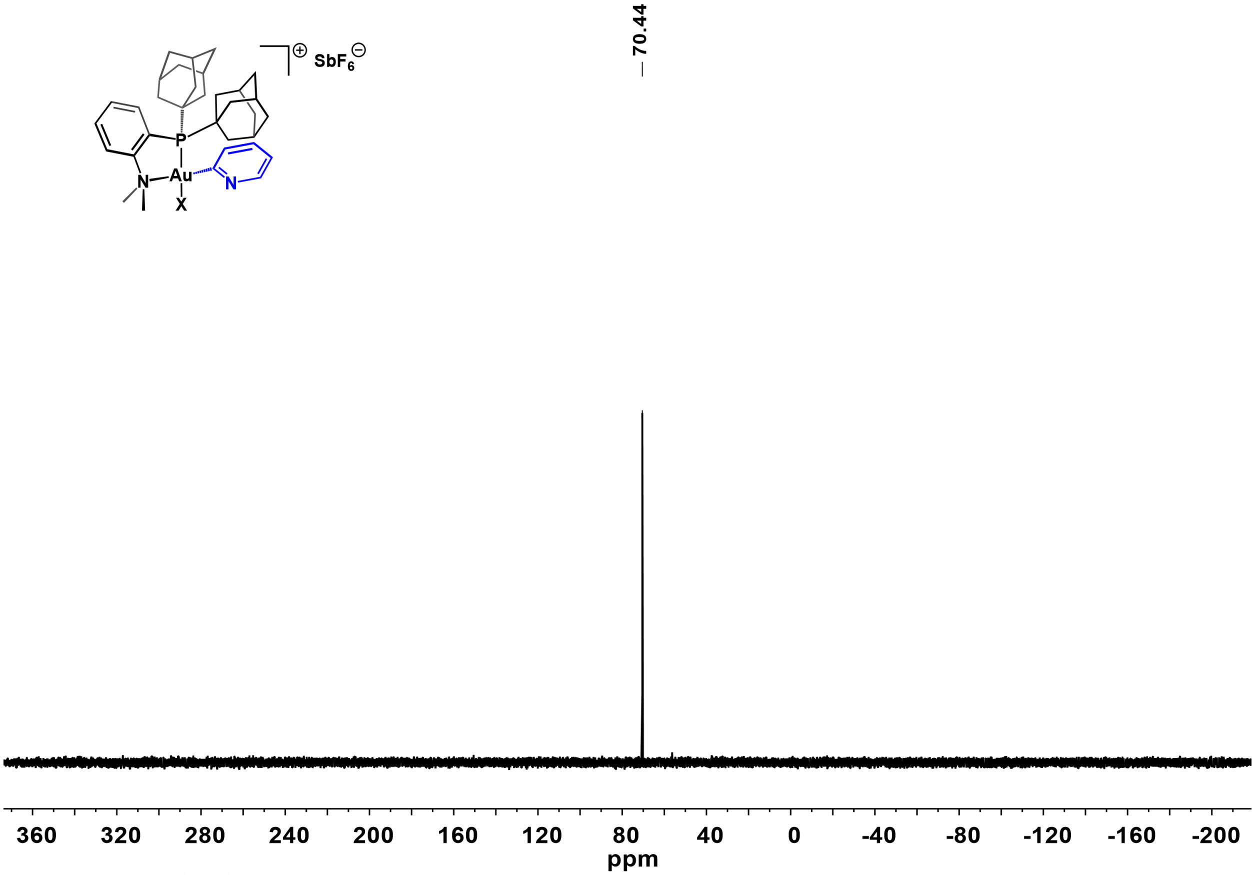


Figure S48. $^{31}P\{^{1}H\}$ NMR spectrum of [**2m**][SbF$_6$] in CD$_3$CN at 298 K.

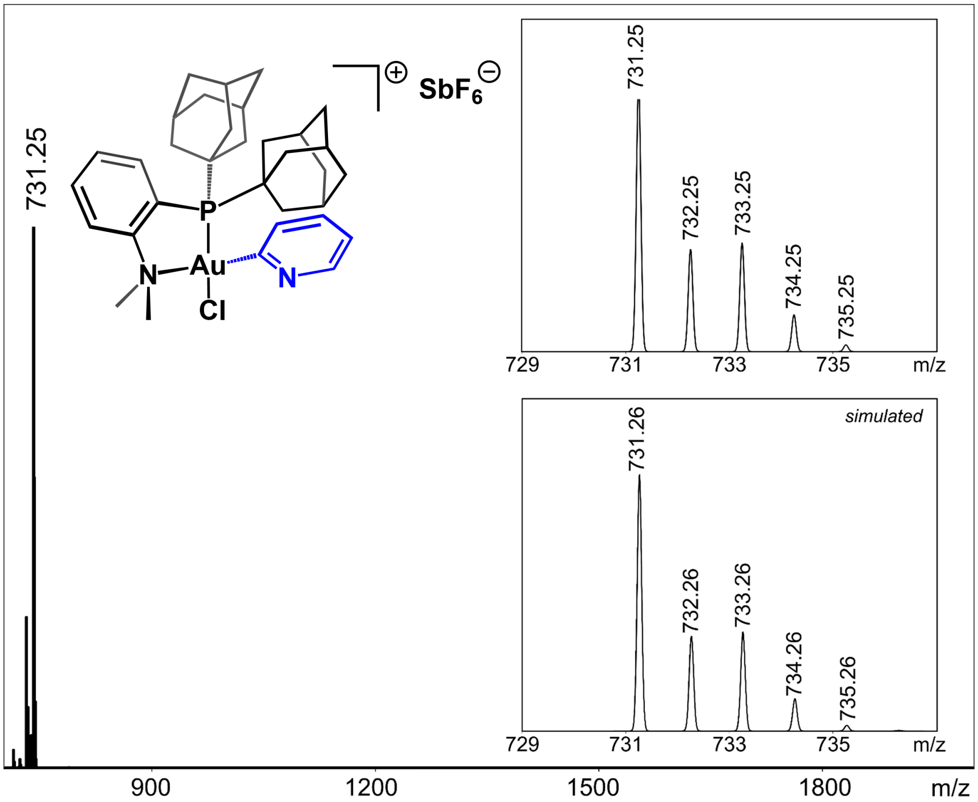
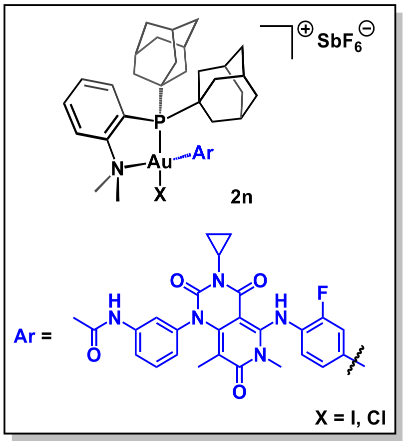


Figure S49. ESI-MS(+) of **2m**.



Following the general procedure, (Me-DalPhos)AuCl (4.23 mg, 0.006 mmol, 1.0 equiv), $AgSbF_6$ (2.22 mg, 0.006 mmol, 1.0 equiv) and Trametinib (19.9 mg, 0.032 mmol, 5.0 equiv) were used. Dichloromethane was removed under reduced pressure after filtration through a pad of Celite to afford a yellow solid. This material was used without further purification.

^{31}P{^{1}H} NMR (162 MHz, CD_3CN): δ 79.7 ppm.

ESI-MS(+): 1141.41 (calc'd 1141.40) *m/z* ($C_{54}H_{63}ClFN_6O_4PAu$).

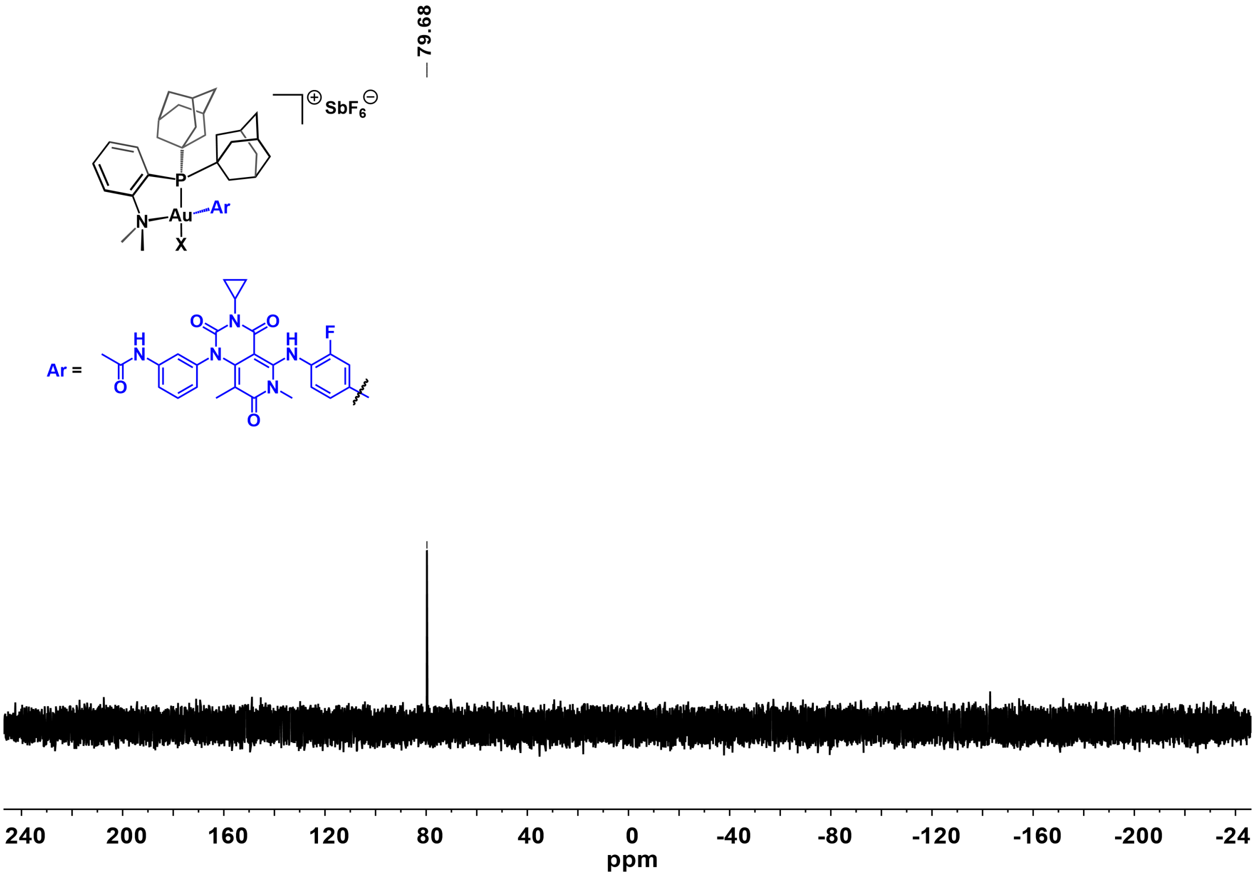


Figure S50. $^{31}P\{^{1}H\}$ NMR spectrum of [**2n**][SbF_6] in CD_3CN at 298 K.

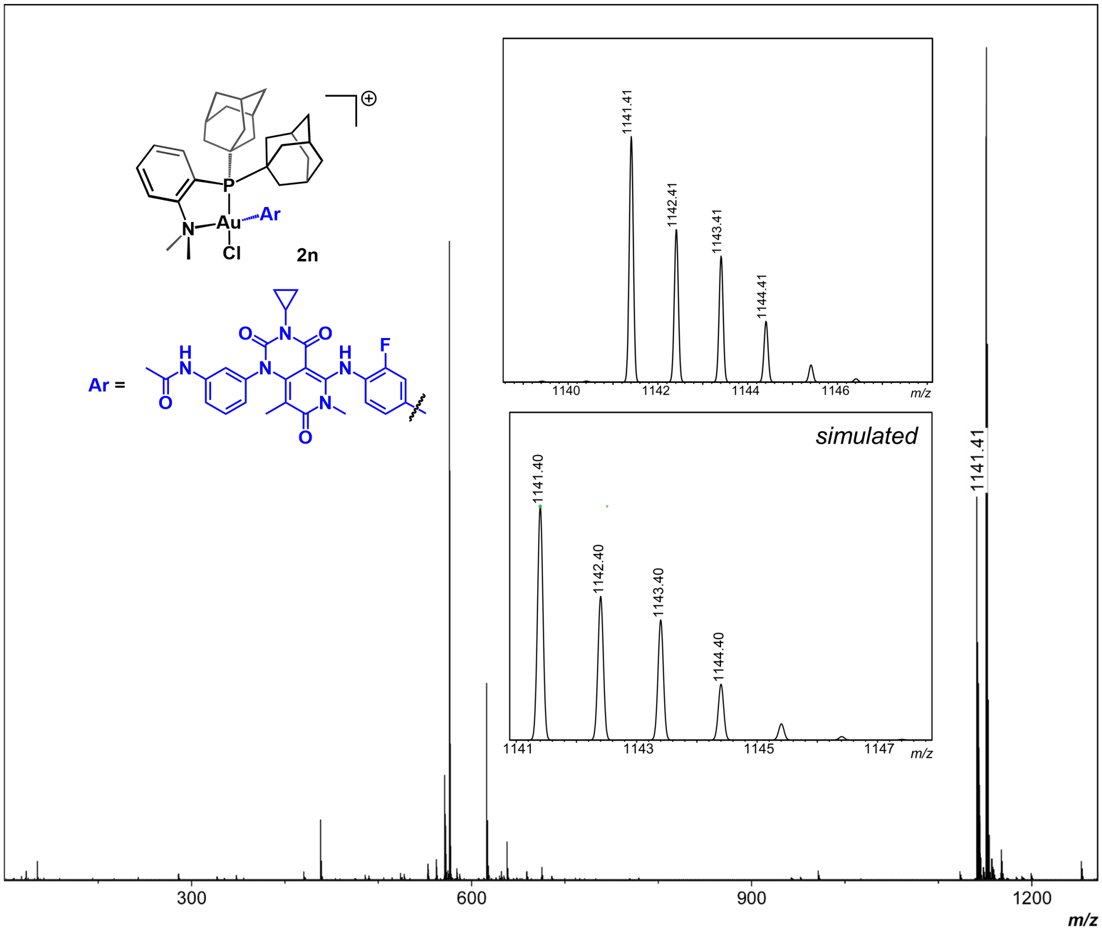
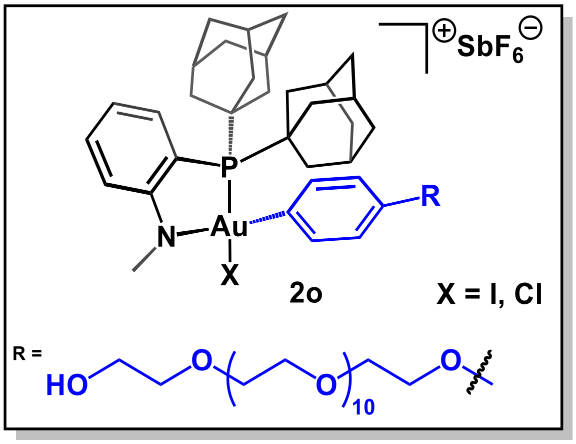


Figure S51. ESI-MS(+) of **2n**.



In the fume hood, $AgSbF_6$ (11 mg, 0.031 mmol, 1.0 equiv) was dissolved in DCM (2 mL) under protection from light, and the colorless solution was cooled to -20 °C. A DCM solution (2 mL) containing **SI-3** (52 mg, 0.078 mmol, 2.5 equiv) and (Me-DalPhos)AuCl (20 mg, 0.031 mmol, 1.0 equiv) reagents was prepared and also cooled to -20 °C. While both solutions were cold, the colorless **SI-3** and (Me-DalPhos)AuCl solution was added in one portion to the solution of $AgSbF_6$. The colorless solution was allowed to stand at 25 °C for 15 min, during which time pale yellow solids precipitated out of solution and a color change to pale yellow was observed. The reaction mixture was filtered through a pad of Celite, and the resulting pale-yellow filtrate was dried under reduced pressure. This material was used without further purification.

$^{31}P\{^{1}H\}$ NMR (162 MHz, CD_3CN): δ 74.3 ppm.

ESI-MS(+): 1262.42 (calc'd 1262.60) *m/z* $(C_{58}H_{93}ClNO_{13}PAu+Na)^+$.

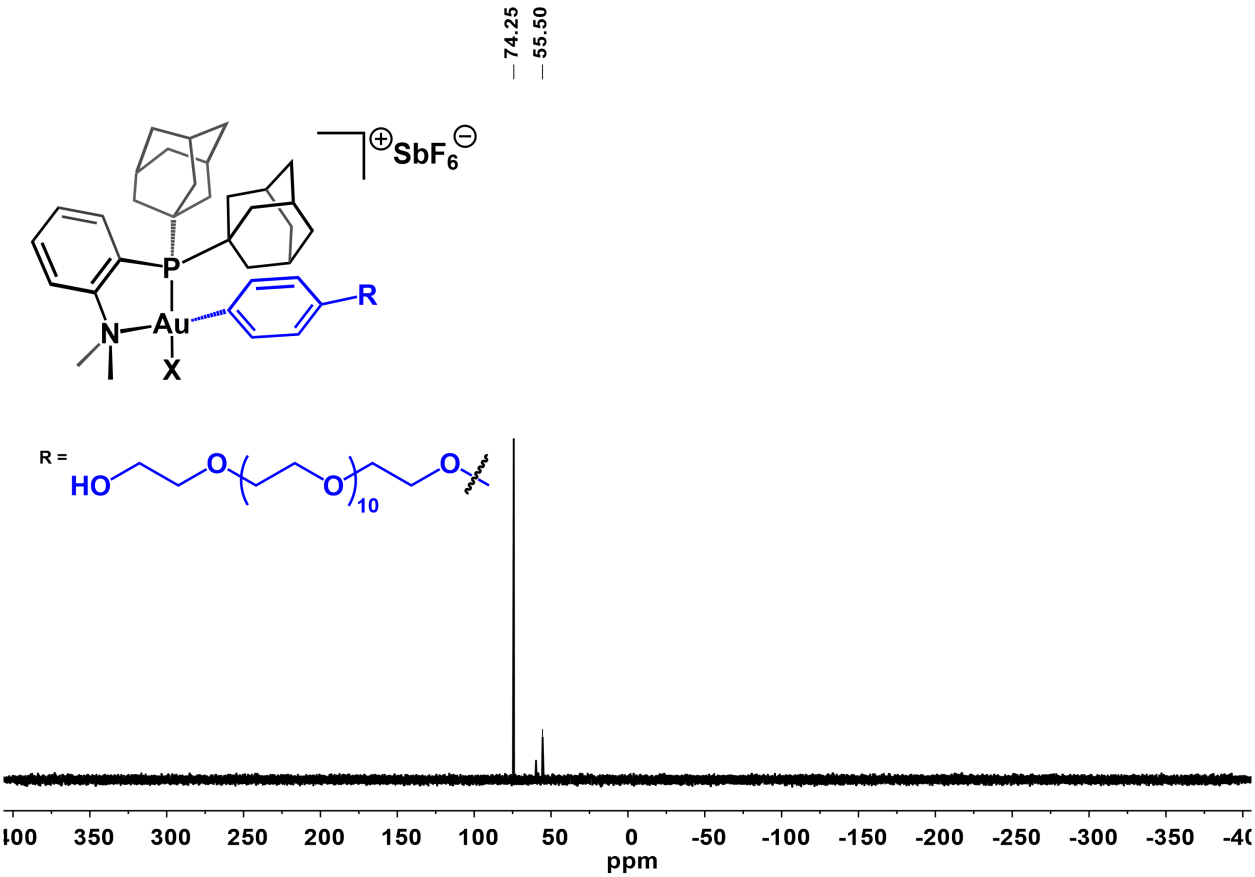


Figure S52. $^{31}P\{^{1}H\}$ NMR spectrum of [**2o**][SbF$_6$] in CD$_3$CN at 298 K.

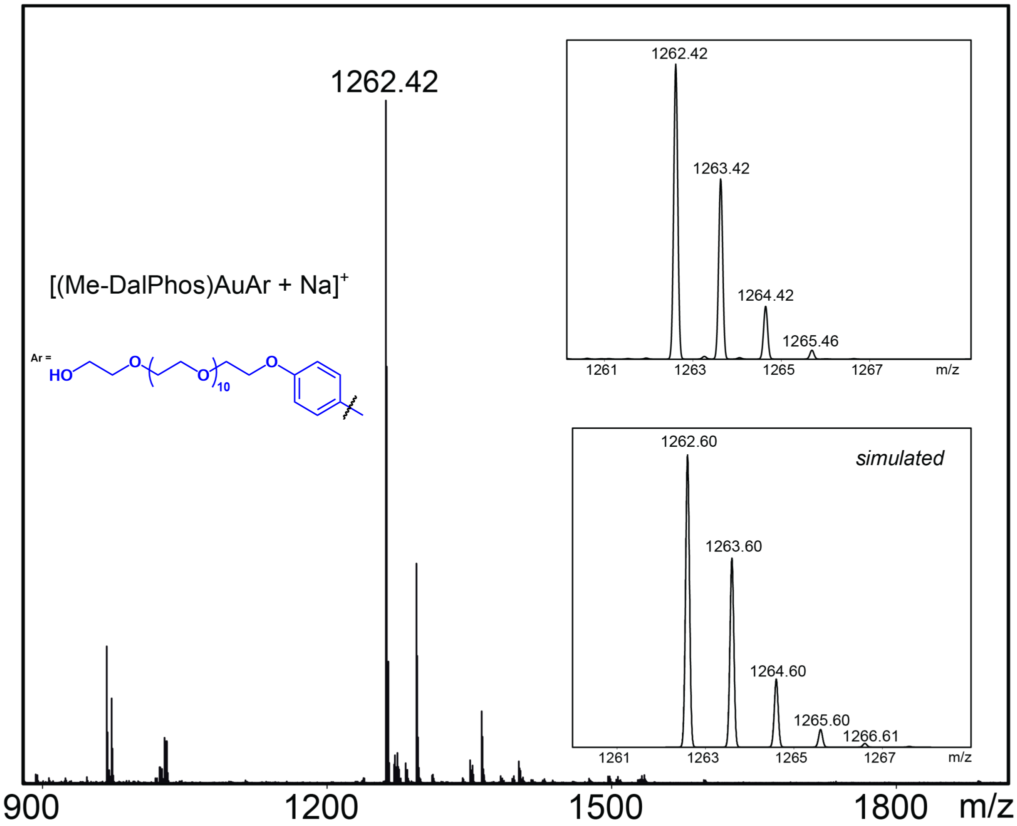
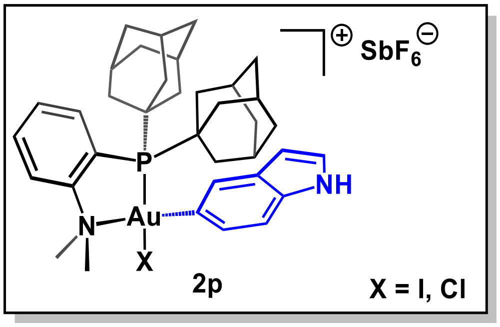


Figure S53. ESI-MS(+) of **2o**.



2p

Following the general procedure, (Me-DalPhos)AuCl (30 mg, 0.046 mmol, 1.0 equiv), $AgSbF_6$ (16 mg, 0.046 mmol, 1.0 equiv) and 5-iodoindole (56 mg, 0.23 mmol, 5.0 equiv) were used. The [**2p**][SbF_6] salt was isolated as a red crystalline solid in 76% yield (35 mg, 0.035 mmol).

^{1}H NMR (400 MHz, CD_3CN): δ 9.61 (s, 1H, -N*H*), 8.07 (m, 1H, H_{Ar}), 8.03–7.92 (m, 2H, H_{Ar}), 7.69 (m, 1H, H_{Ar}), 7.48 (d, 1H, *J* = 7.6 Hz, H_{Ar}), 7.39 (d, 1H, *J* = 7.7 Hz, H_{Ar}), 7.02 (t, 1H, *J* = 7.7 Hz, -CHC*H*NH-), 6.52 (dd, 1H, *J* = 3.2 Hz, 2.0 Hz, -C*H*CHNH-), 3.58 (s, 3H, $N(CH_3)_2$), 3.52 (s, 3H, $N(CH_3)_2$), 2.36 (s, 4H, H_{Ad}), 2.24 (s, 4H, H_{Ad}), 2.00 (s, 3H, H_{Ad}), 1.84 (s, 4H, H_{Ad}), 1.70 (s, 10H, H_{Ad}), 1.54 (s, 5H, H_{Ad}) ppm.

^{31}P{^{1}H} NMR (162 MHz, CD_3CN): δ 80.7 ppm.

ESI-MS(+): 769.20 (calc'd 769.28) *m/z* ($C_{36}H_{46}ClN_2PAu$).

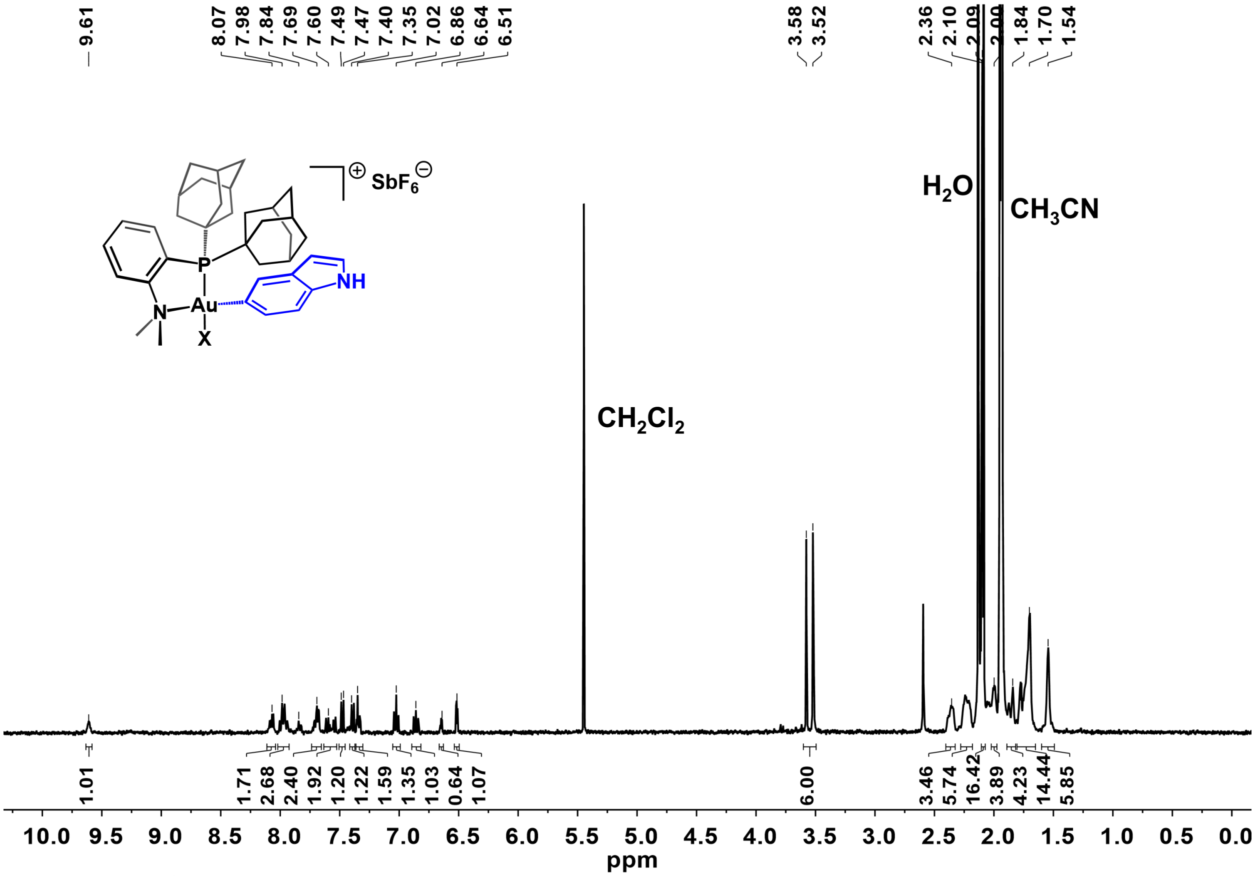


Figure S54. ^{1}H NMR spectrum of [**2p**][SbF$_6$] in CD$_3$CN at 298 K.

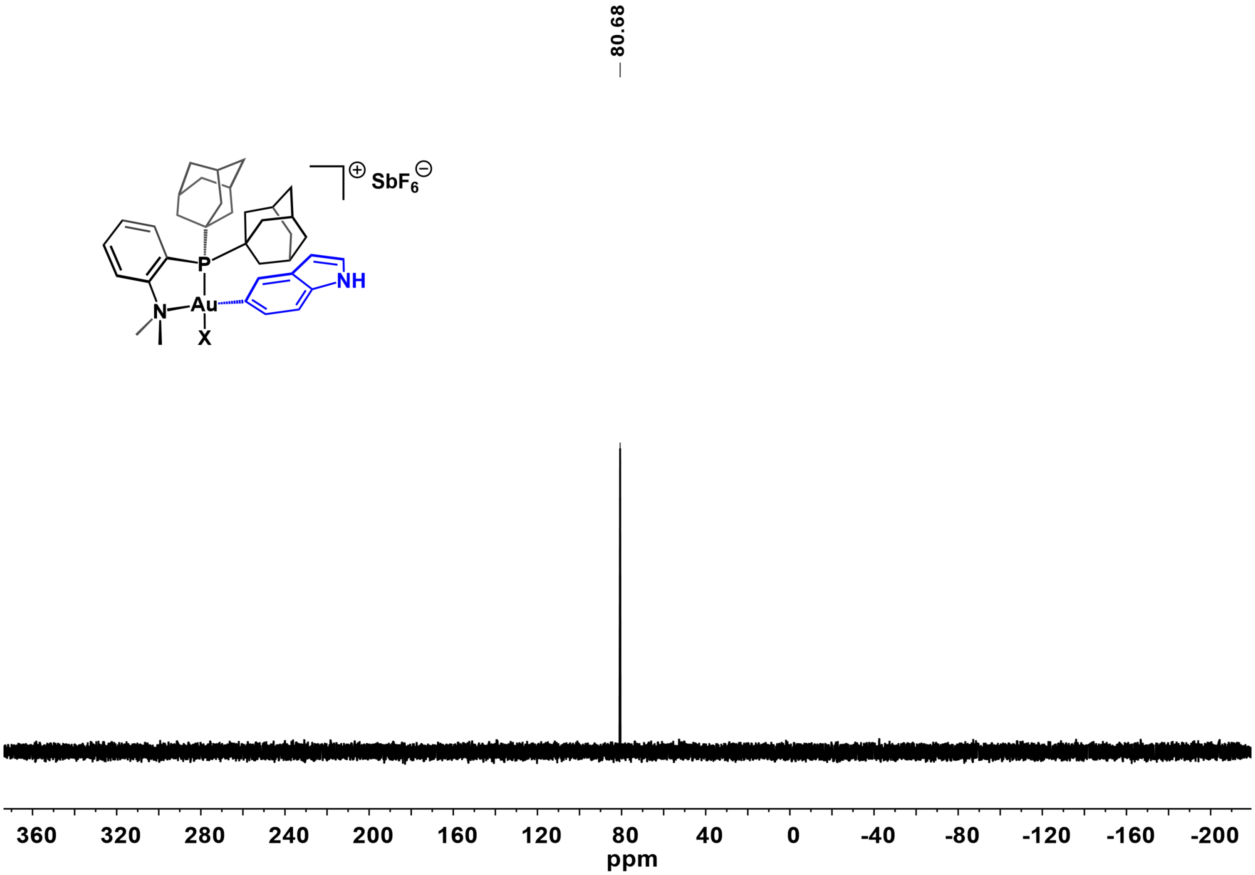


Figure S55. ^{31}P{^{1}H} NMR spectrum of [**2p**][SbF$_6$] in CD$_3$CN at 298 K.

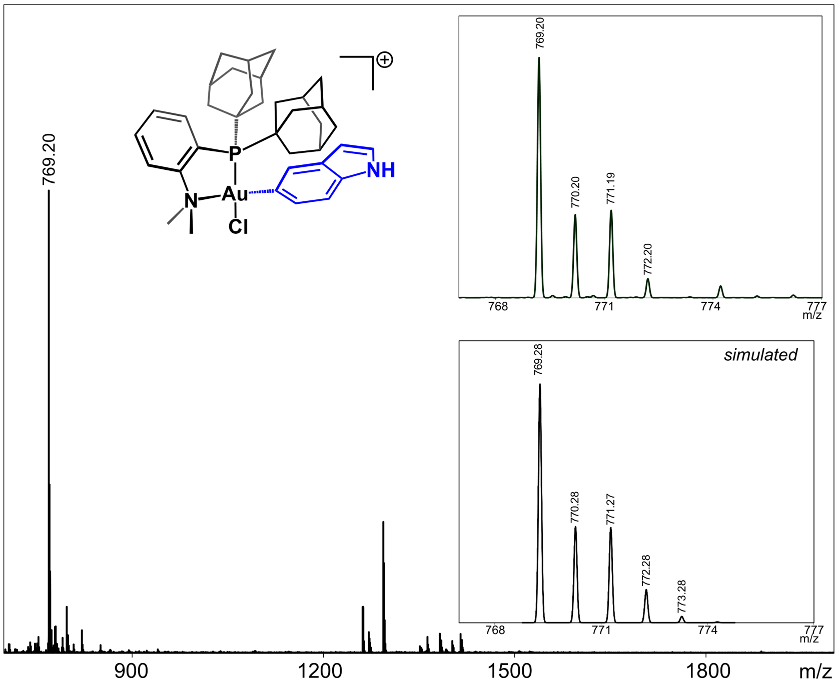
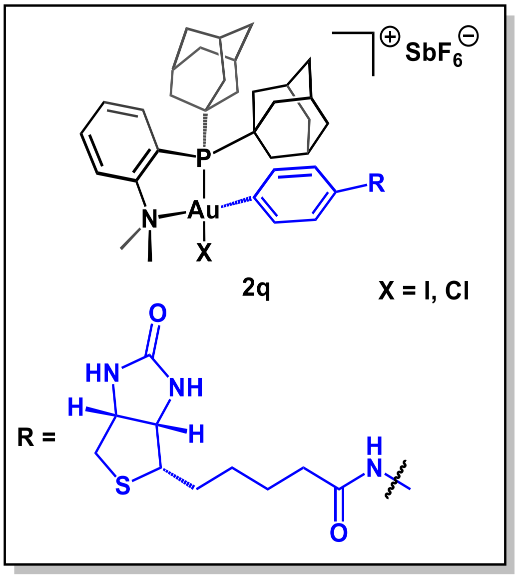


Figure S56. ESI-MS(+) of **2p**.



2q

In the fume hood, AgSbF$_6$ (3 mg, 0.009 mmol, 1 equiv) was dissolved in DCM (2 mL) under protection from light, and the colorless solution was cooled to -20 °C. A DCM suspension (2 mL) containing **SI-1** (6 mg, 0.01 mmol, 1 equiv) and (Me-DalPhos)AuCl (6 mg, 0.009 mmol, 1 equiv) reagents was prepared and also cooled to -20 °C. While both solutions were cold, the colorless **SI-1** and (Me-DalPhos)AuCl suspension was added in one portion to the solution of AgSbF$_6$. The colorless suspension was sonicated for 1 min, and then the reaction mixture was filtered through a pad of Celite. The resulting pale-yellow filtrate was dried under reduced pressure. This material was used without further purification.

^{31}P{^{1}H} NMR (162 MHz, CD$_3$CN): δ 74.7 ppm.

ESI-MS(+): 971.27 (calc'd 971.35) *m/z* ($C_{44}H_{60}ClN_4O_2PSAu$).

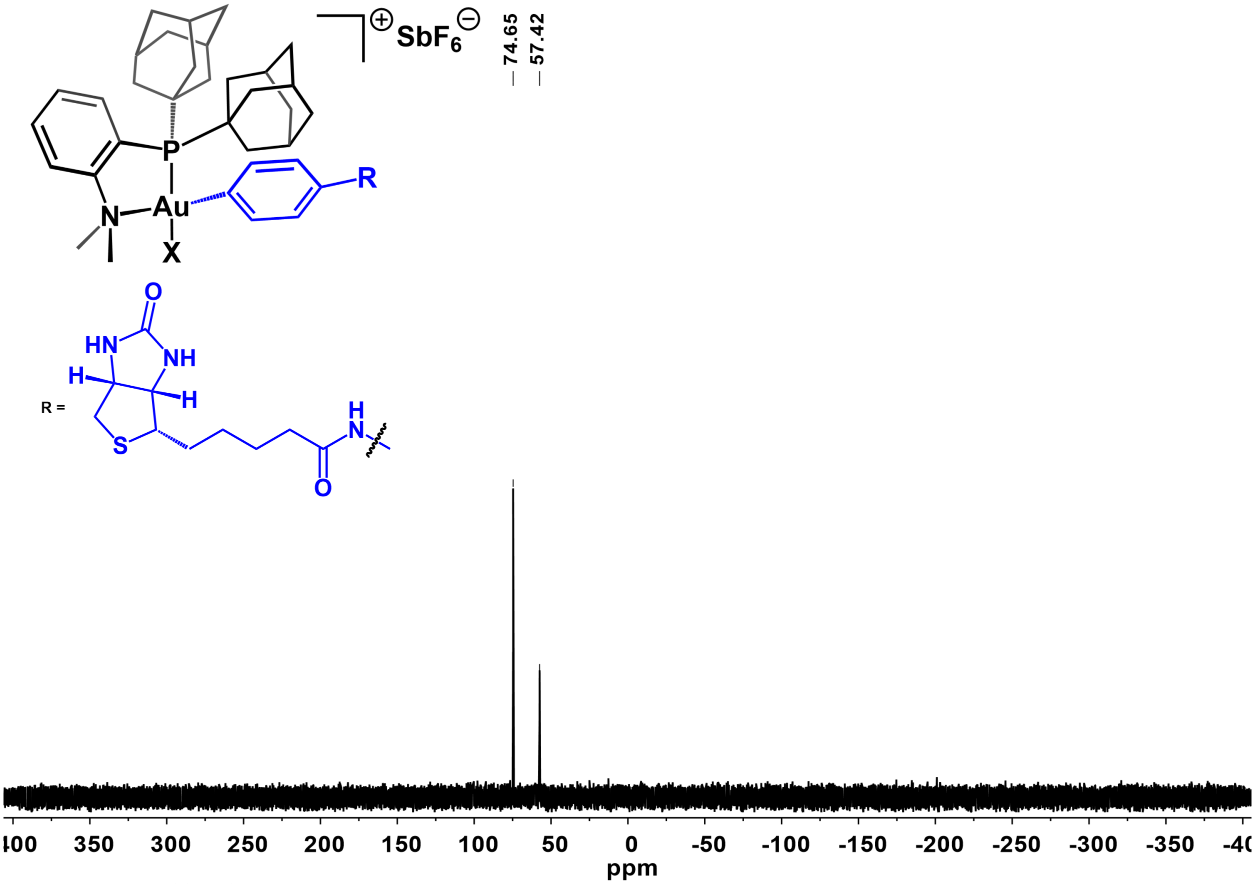


Figure S57. $^{31}P\{^{1}H\}$ NMR spectrum of [**2q**][SbF$_6$] in CD$_3$CN at 298 K. The signal at 57.4 ppm corresponds to the starting (Me-DalPhos)AuCl compound.

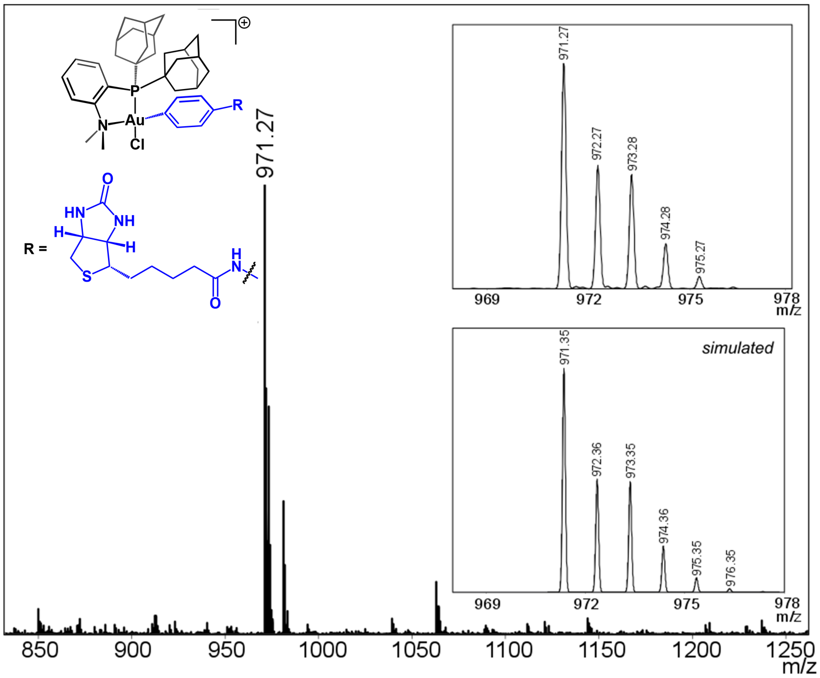
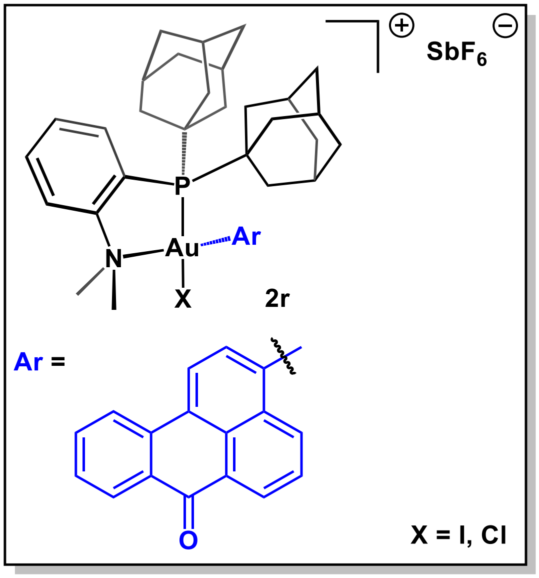


Figure S58. ESI-MS(+) of **2q**.



Following the general procedure, (Me-DalPhos)AuCl (16 mg, 0.024 mmol, 1.0 equiv), $AgSbF_6$ (8 mg, 0.02 mmol, 1 equiv) and 3-iodobenzanthrone (13 mg, 0.36 mmol, 1.5 equiv) were used. The [**2g**][SbF_6] salt was isolated as an orange crystalline solid in 31% yield (8 mg, 0.007). A single crystal of suitable quality for an X-ray diffraction study was obtained using this procedure (See section V for crystallographic details).

^{1}H NMR (400 MHz, CD_3CN): δ 8.79 (d, 1H, J = 7.2, H_{Ar}), 8.62 (t, 2H, J = 7.6 Hz, H_{Ar}), 8.55 (d, 1H, J = 8.0 Hz, H_{Ar}), 8.45 (dd, 1H, J = 7.9 Hz, 1.4 Hz, H_{Ar}), 8.22 (d, 1H, J = 8.2 Hz, H_{Ar}), 8.14 (m, 1H, H_{Ar}), 8.08 (m, 2H, H_{Ar}), 7.95 – 7.85 (m, 1H, H_{Ar}), 7.70 (t, 2H, J = 7.5 Hz, H_{Ar}), 3.67 (s, 3H, $N(CH_3)_2$), 3.64 (s, 3H, $N(CH_3)_2$), 2.49 (s, 4H, H_{Ad}), 2.34 (s, 4H, H_{Ad}), 2.20 (s, 3H, H_{Ad}), 1.86 (s, 4H, H_{Ad}), 1.77 (s, 4H, H_{Ad}), 1.70 (4H, s, H_{Ad}), 1.45 (s, 7H, H_{Ad}) ppm.

^{31}P{^{1}H} NMR (162 MHz, CD_3CN): δ 89.9 ppm.

ESI-MS(+): 892.31 (calc'd 892.33) *m/z*.
Note this sample was run in the presence of formic acid, and as a result, the [(Me-DalPhos)Au(benzanthrone)OCHO]$^+$ ion is observed ($C_{46}H_{50}NPO_3Au$).

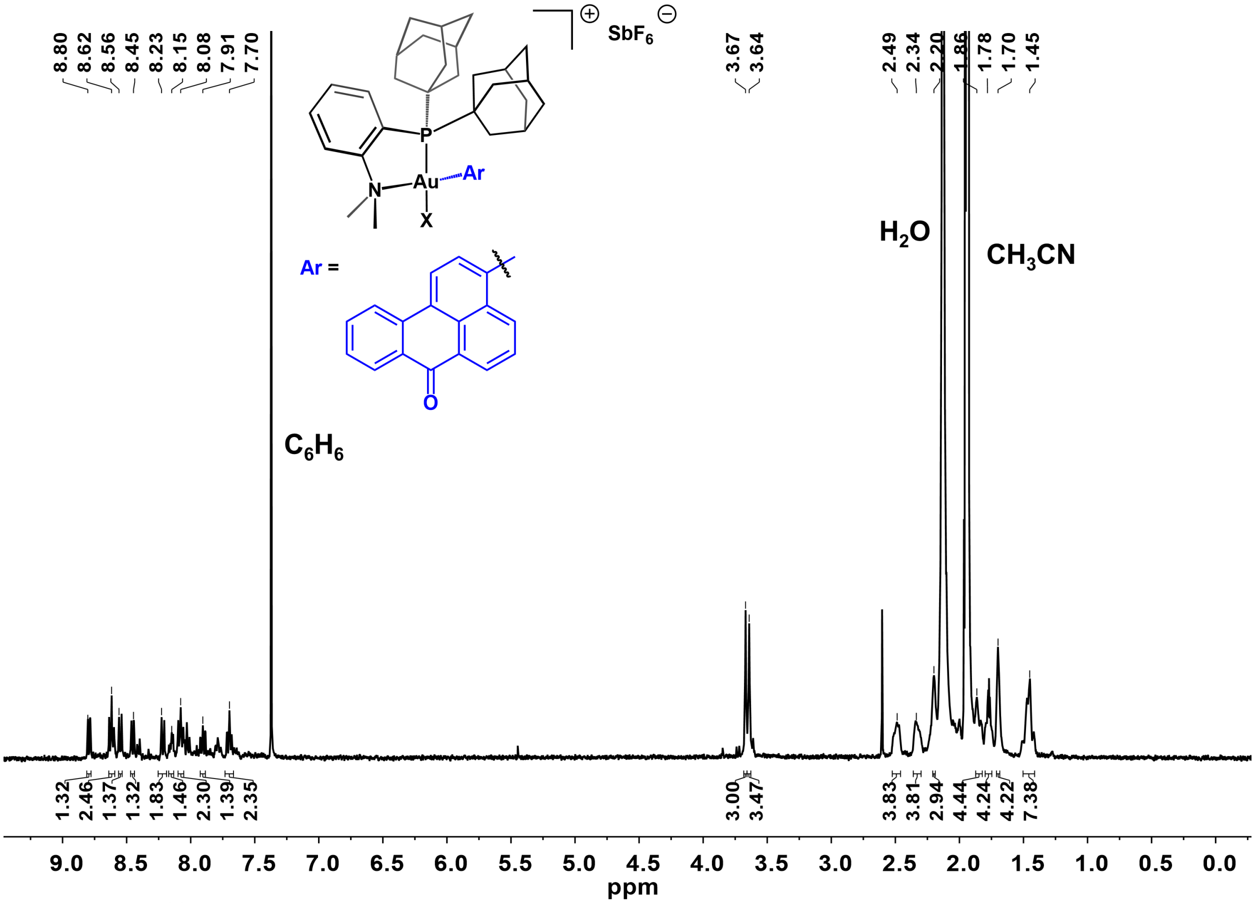


Figure S59. ^{31}P NMR spectrum of [**2r**][SbF$_6$] in CD$_3$CN at 298 K.

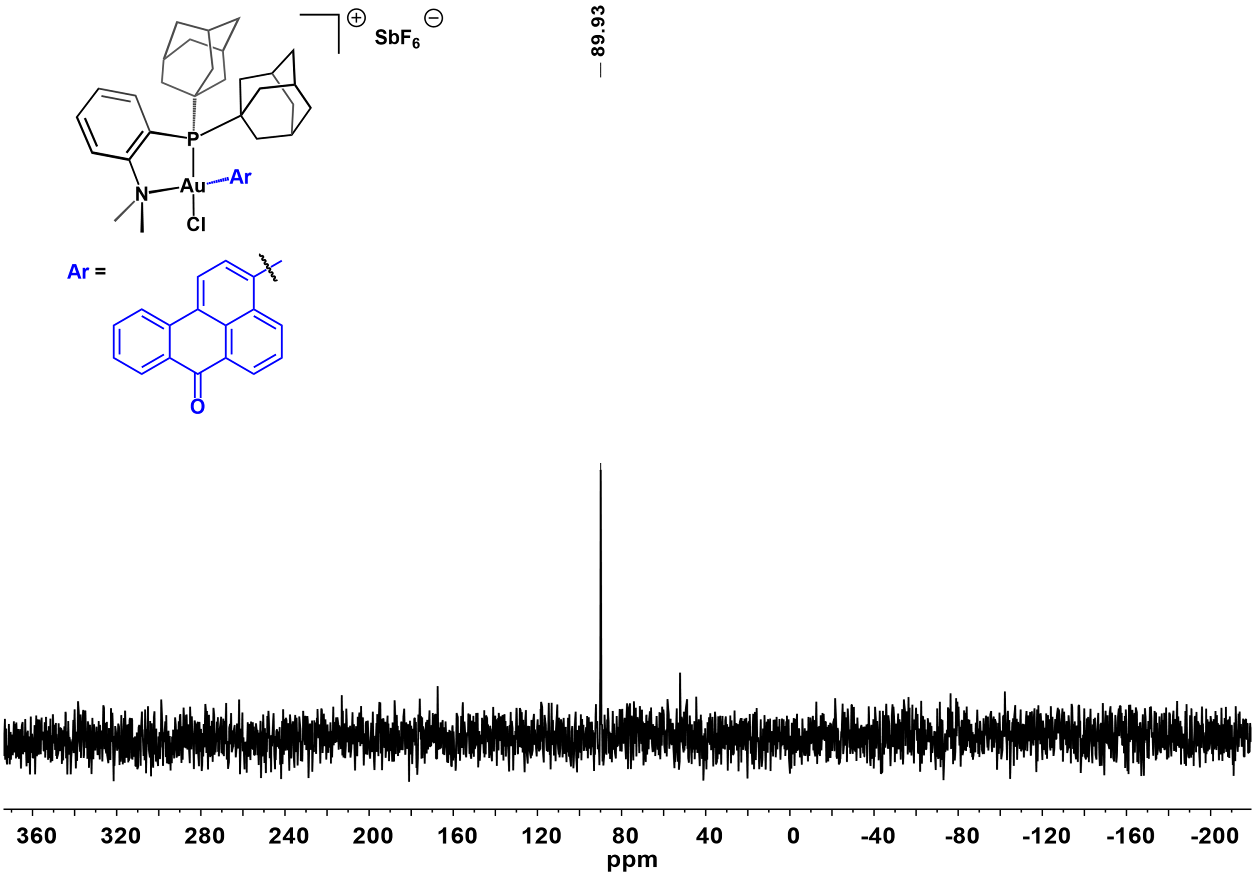


Figure S60. $^{31}P\{^{1}H\}$ NMR spectrum of [**2r**][SbF$_6$] in CD$_3$CN at 298 K.

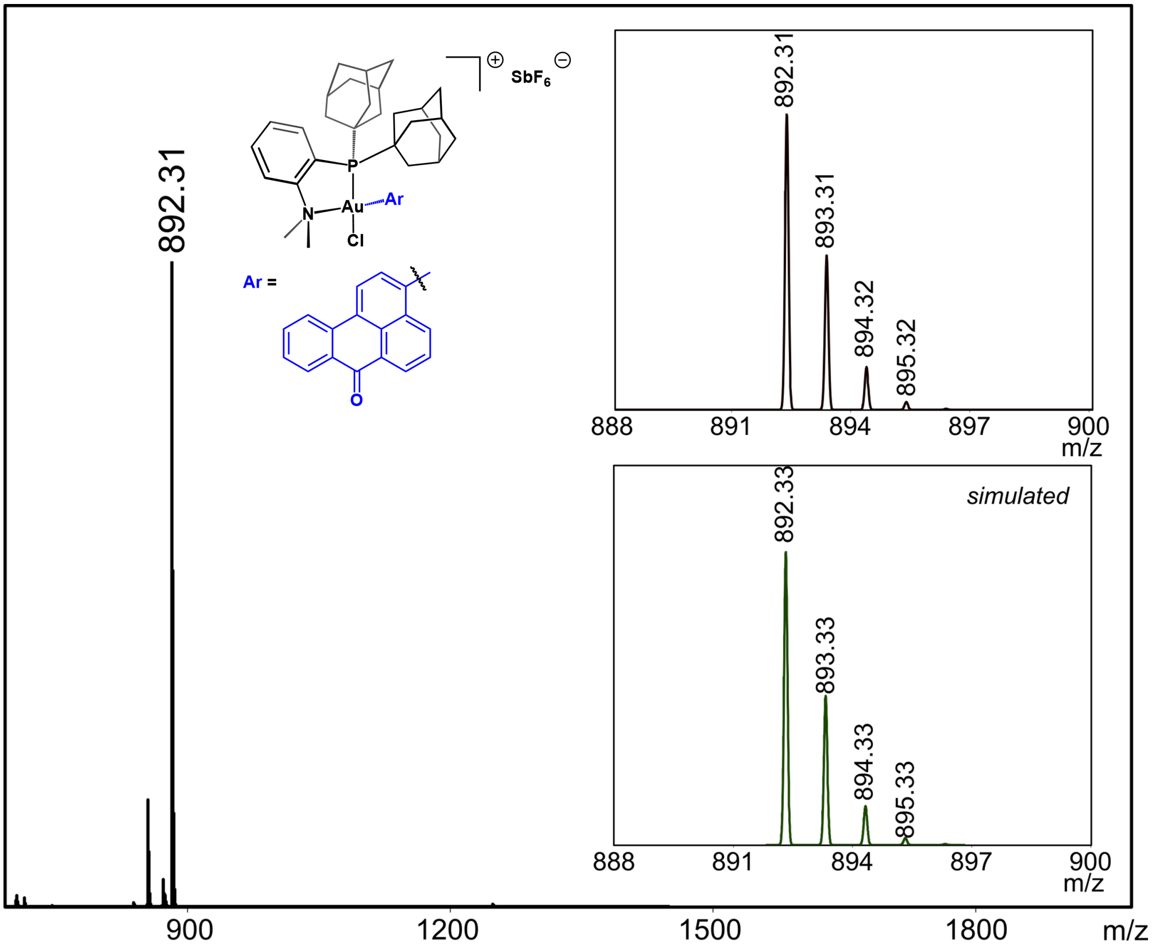
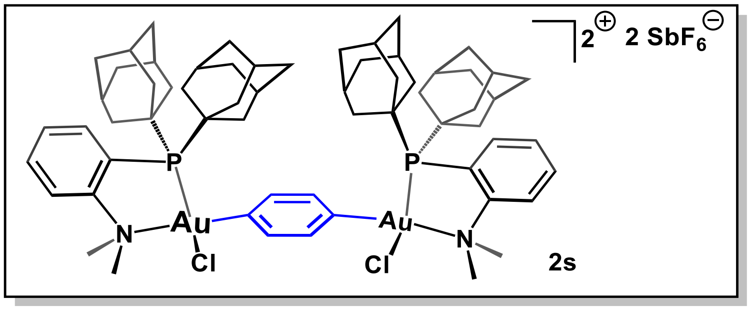


Figure S61. ESI-MS(+) of **2r**. Note this sample was run in the presence of formic acid.



2s

In the fume hood, $AgSbF_6$ (16 mg, 0.046 mmol, 2.2 equiv) was dissolved in DCM (2 mL) under protection from light, and the colorless solution was cooled to -20 °C. A DCM solution (2 mL) containing 1,4-diiodobenzene (7 mg, 0.02 mmol, 1 equiv) and (Me-DalPhos)AuCl (30 mg, 0.046 mmol, 2.2 equiv) reagents was prepared and also cooled to -20 °C. While both solutions were cold, the colorless 1,4-diiodobenzene and (Me-DalPhos)AuCl solution was added in one portion to the solution of $AgSbF_6$, resulting in an immediate color change to bright yellow concomitant with precipitation of pale yellow solids. The reaction mixture was filtered through a pad of Celite, and the resulting yellow filtrate was allowed to stand undisturbed at 25 °C for 48 h, during which time the [**2s**][SbF_6]$_2$ product crystallized from solution. The pale-yellow supernatant was decanted, and the yellow crystals were washed with C_6H_6 (3 × 2 mL). The crystals were then washed with *n*-pentane (3 mL) and dried under reduced pressure to afford [**2s**][SbF_6]$_2$ as a yellow crystalline solid in 67% yield (24 mg, 0.013 mmol). A crystal of suitable quality for an X-ray diffraction study was obtained using this procedure. The X-ray crystallographic analysis indicated **2s** crystallized with 100% Cl occupancy (see section V).

^{1}H NMR (400 MHz, CD_3CN): δ 8.08–8.04 (m, 2H, H_{Ar}), 8.02–7.91 (m, 4H, H_{Ar}), 7.70 (m, 2H, H_{Ar}), 7.53 (s, 4H, H_{Ar}), 3.50 (s, 12H, $N(CH_3)_2$), 2.28 (d, *J* = 8.8 Hz, 12H, H_{Ad}), 2.09 (s, 12H, H_{Ad}), 2.04–1.99 (m, 11H, H_{Ad}), 1.74 (m, 25H, H_{Ad}) ppm.

$^{31}P\{^1H\}$ NMR (162 MHz, CD_3CN): δ 78.6 ppm.

ESI-MS: 691.17 (calc'd 691.24) *m/z* for $C_{62}H_{84}Cl_2N_2P_2Au_2$.

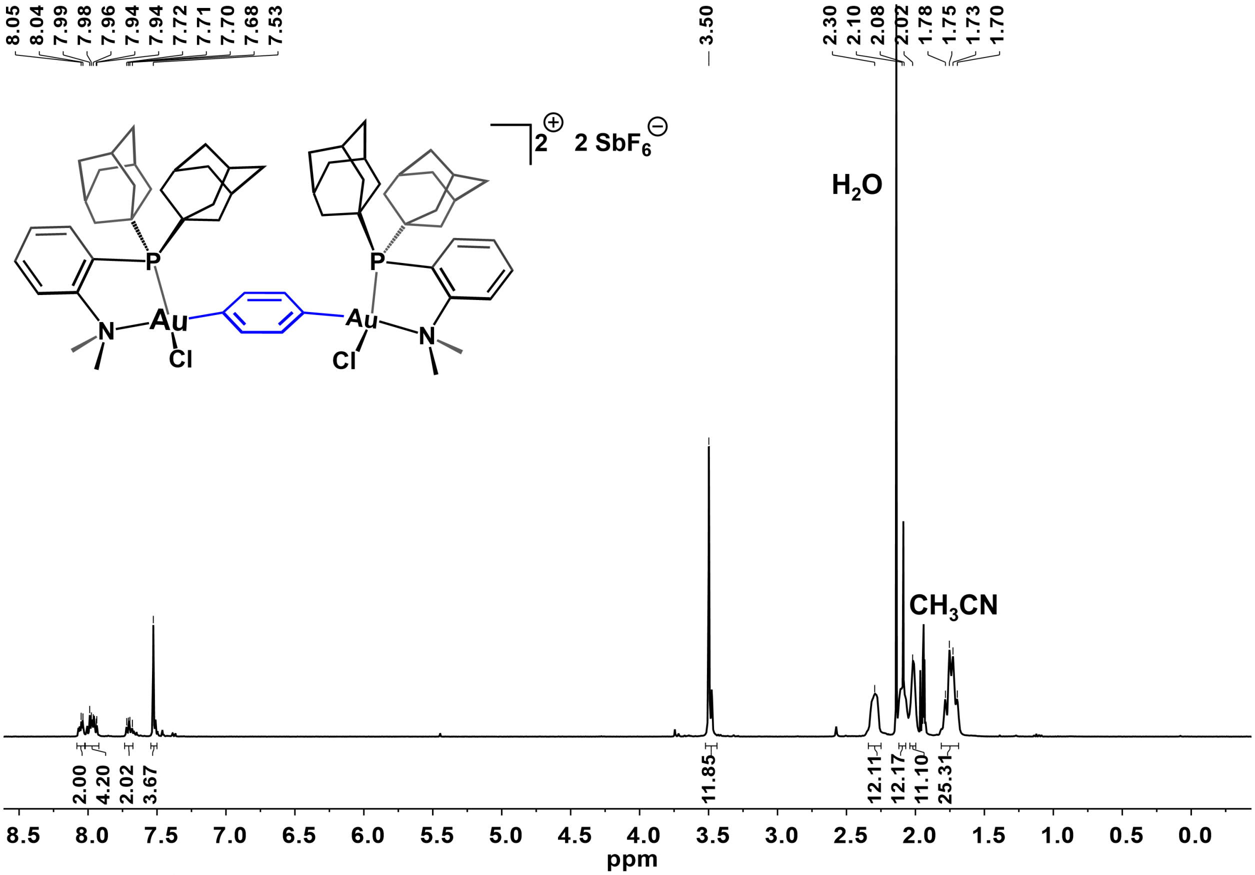


Figure S62. ^{1}H NMR spectrum of [**2s**][SbF$_6$]$_2$ in CD$_3$CN at 298 K.

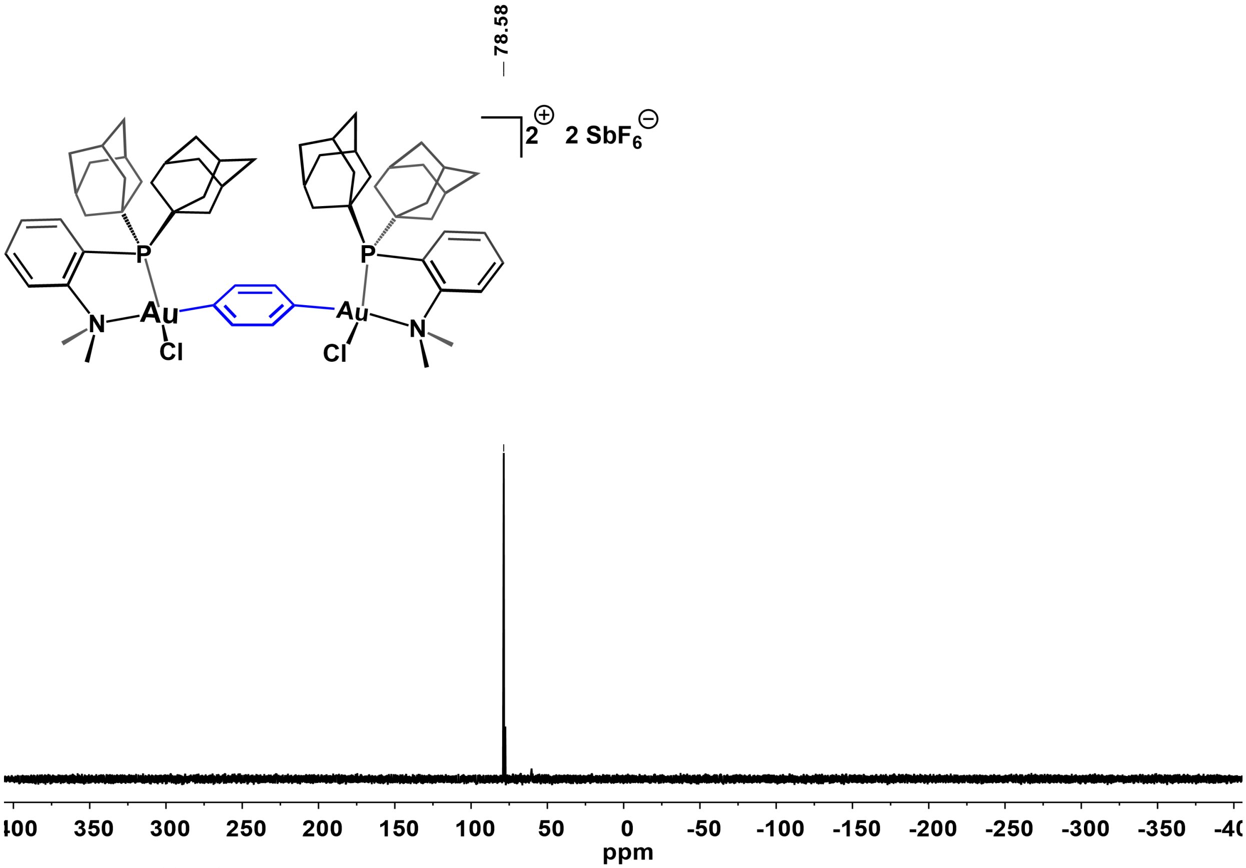


Figure S63. $^{31}P\{^{1}H\}$ NMR spectrum of [**2s**][SbF$_6$]$_2$ in CD$_3$CN at 298K.

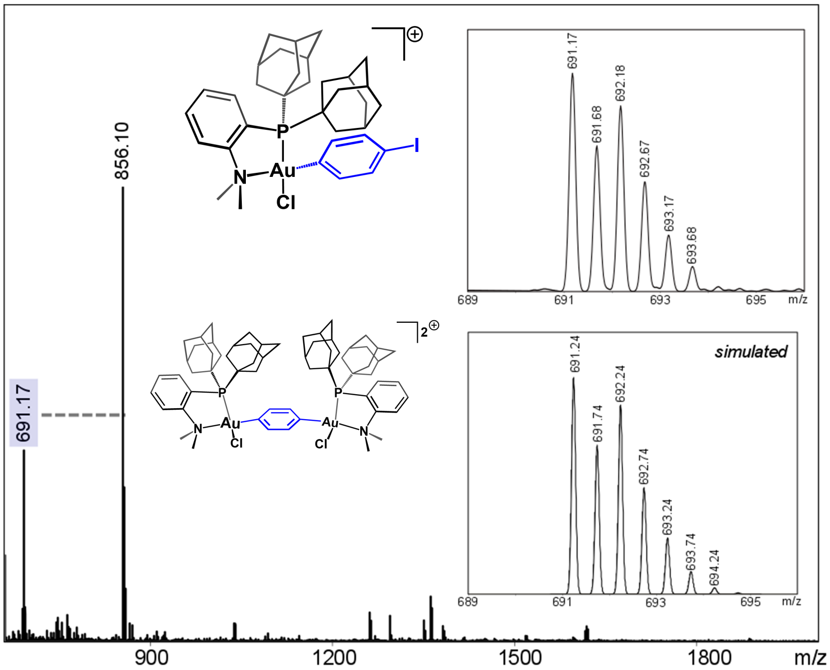


Figure S64. ESI-MS(+)of **2s**.

Stability studies of complexes [2a][SbF$_6$] and [2c][SbF$_6$].

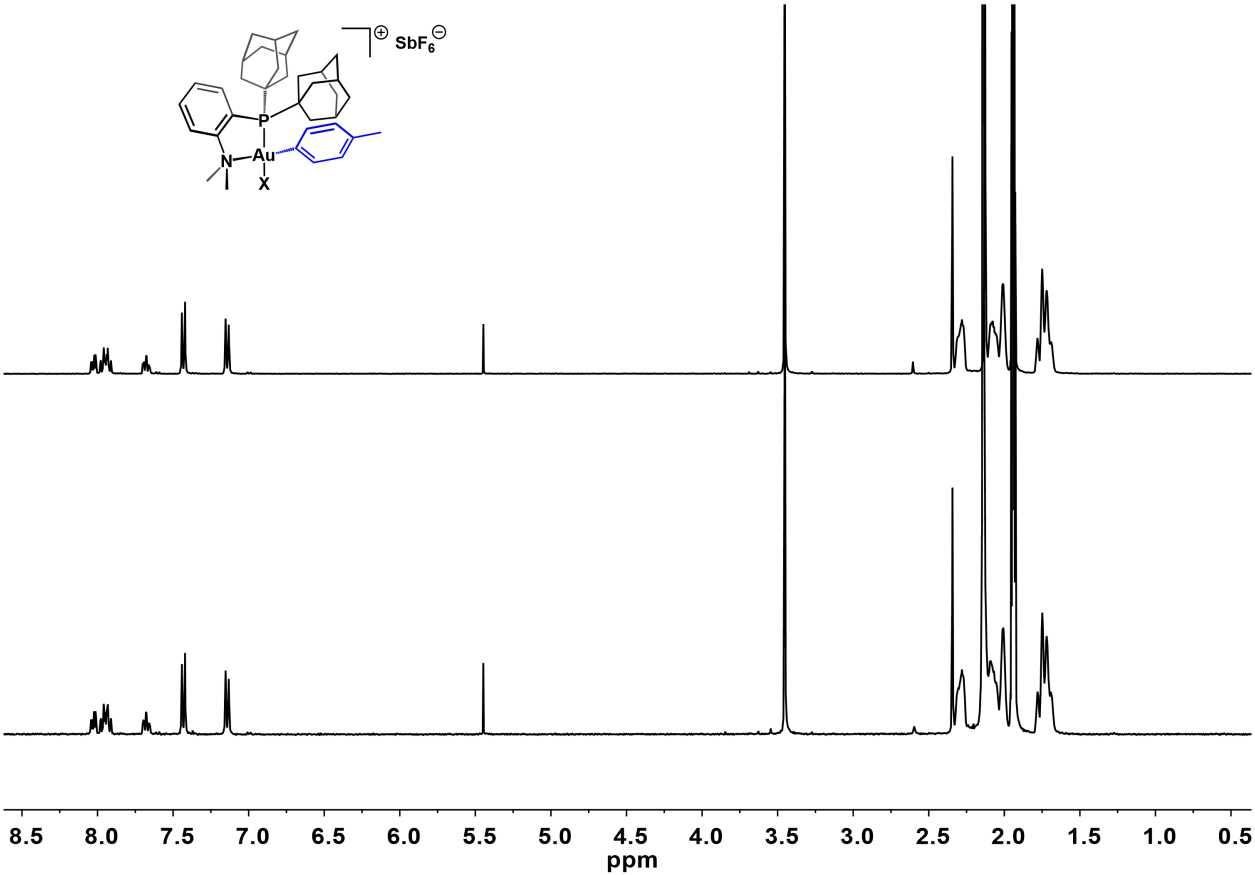


Figure S65. ^{1}H NMR spectrum of a newly prepared sample of [**2a**][SbF$_6$] (top) and spectrum of the same sample after storage as a solid for two months at 25 °C (bottom). Spectra collected in CD$_3$CN, 298 K.

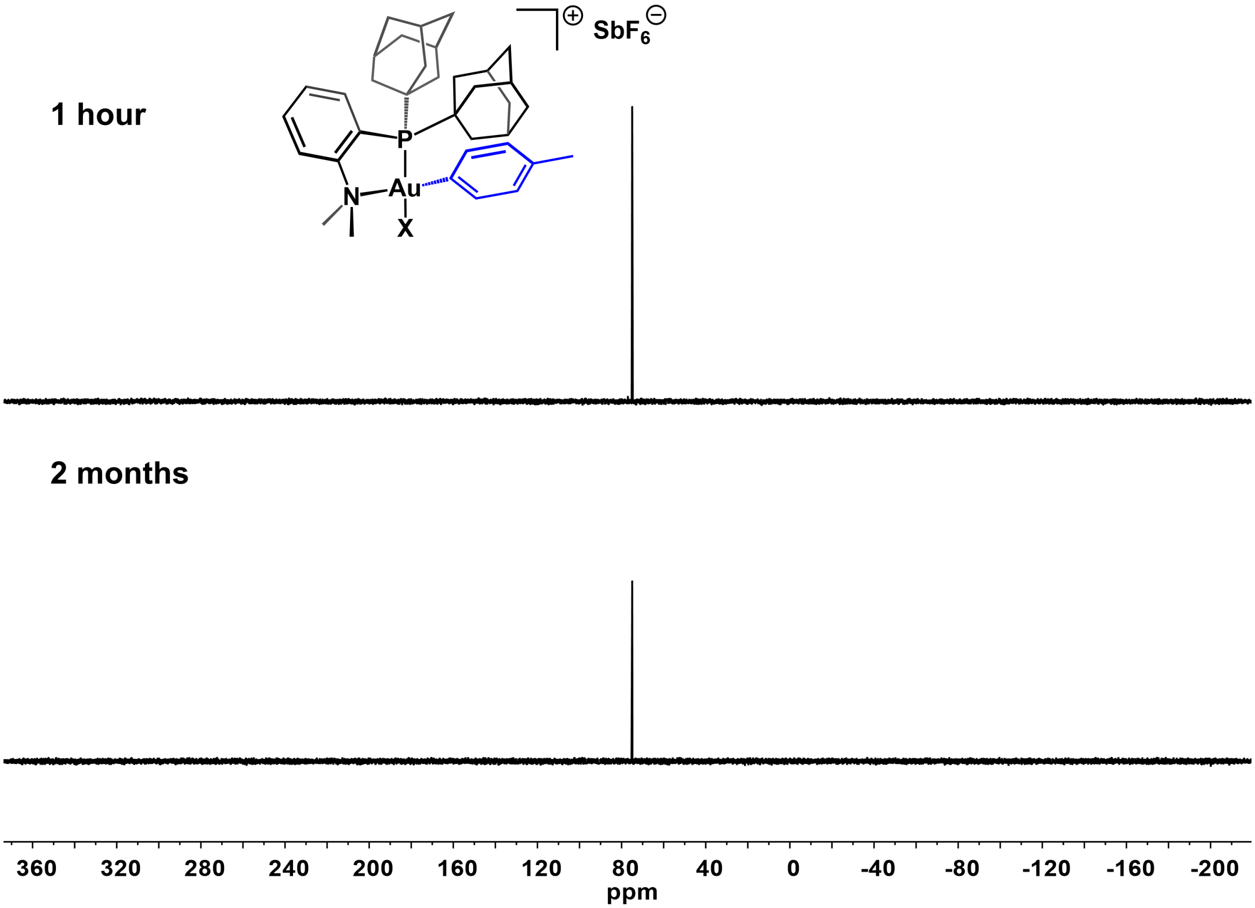


Figure S66. $^{31}P\{^1H\}$ NMR spectrum of a newly prepared sample of [**2a**][SbF_6] (top) and spectrum of the same sample after storage as a solid for two months at 25 °C (bottom). Spectra collected in CD_3CN, 298 K.

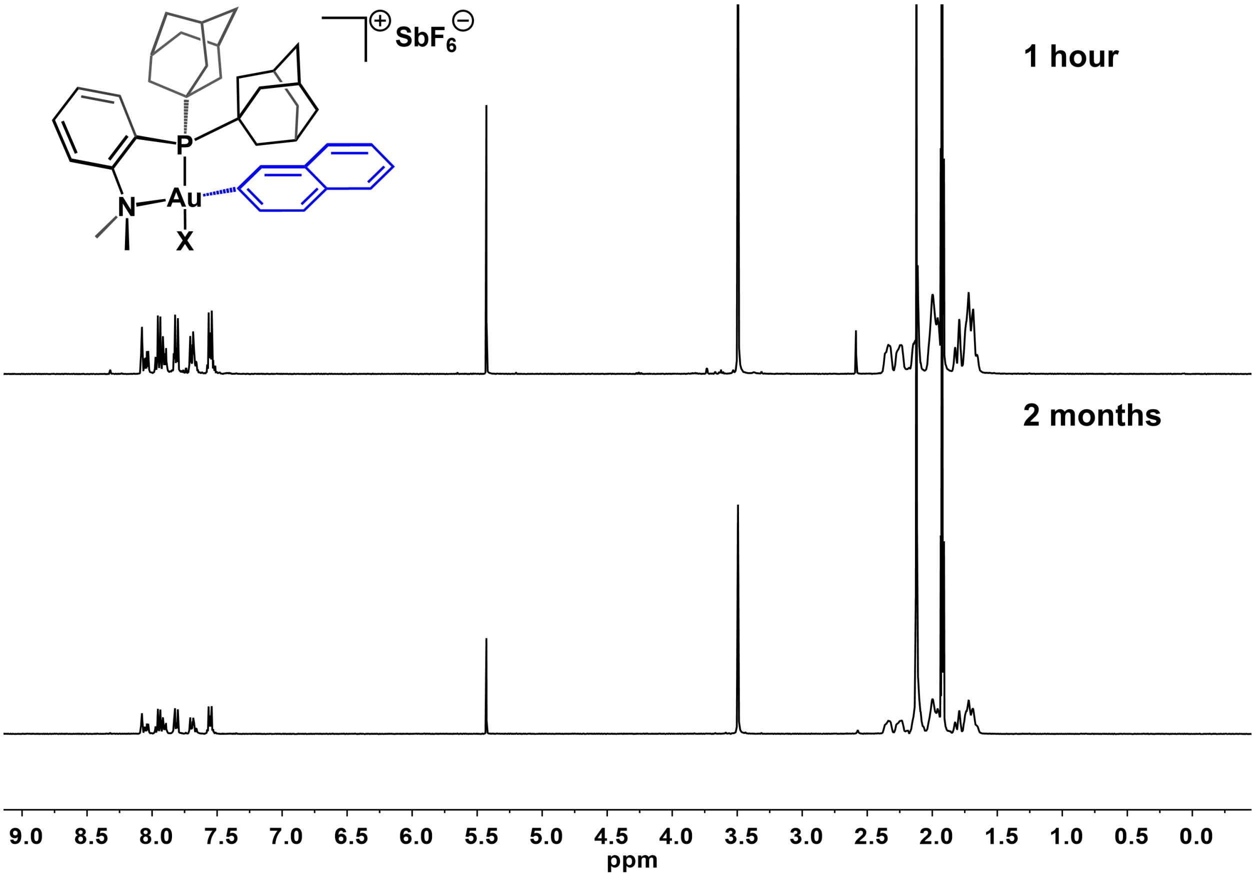


Figure S67. ^{1}H NMR spectrum of a newly prepared sample of [**2c**][SbF$_6$] (top) and spectrum of the same sample after storage as a solid for two months at 25 °C (bottom). Spectra collected in CD$_3$CN at 298 K.

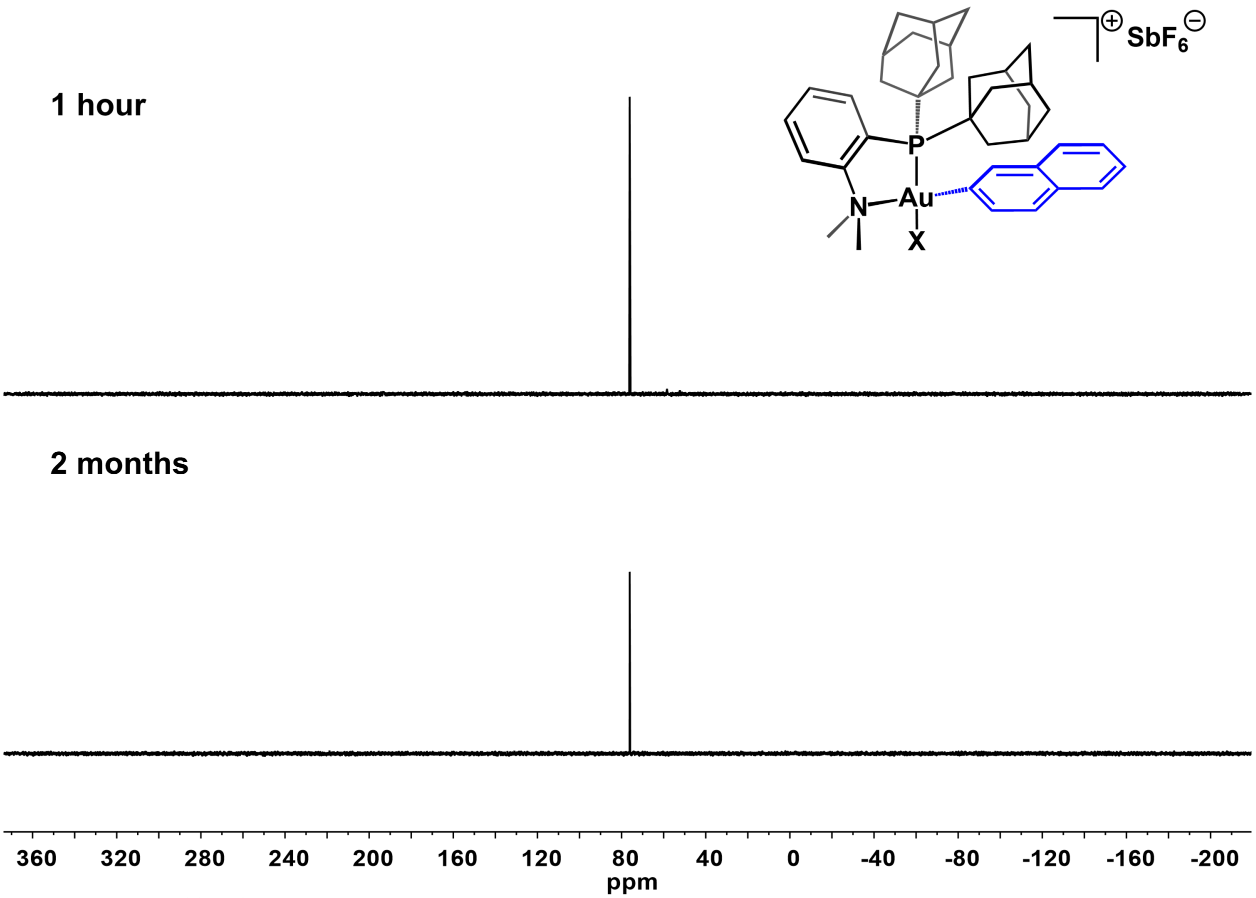


Figure S68. $^{31}P\{^{1}H\}$ NMR spectrum of a newly prepared sample of [**2c**][SbF_6] (top) and spectrum of the same sample after storage as a solid for two months at 25 °C (bottom). Spectra collected in CD_3CN at 298 K.

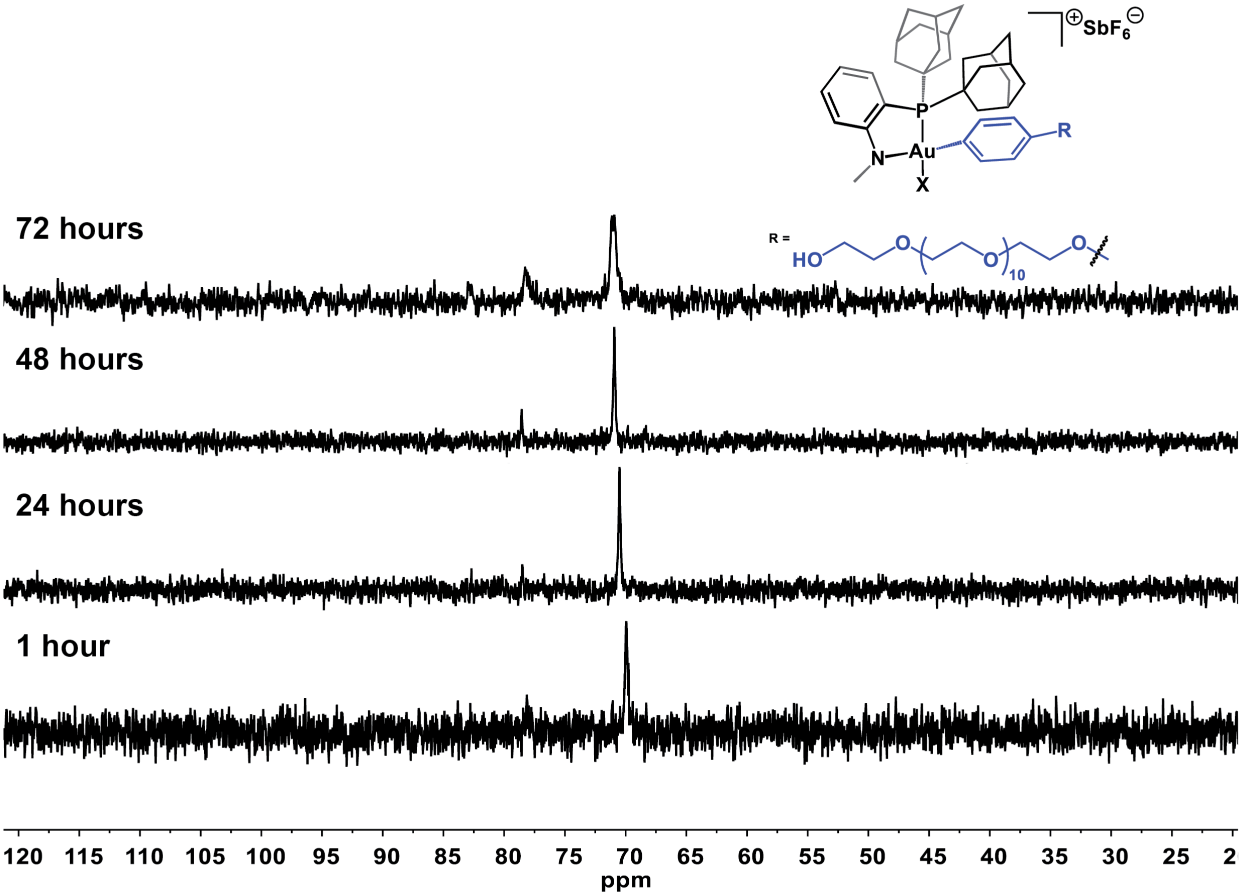


Figure S69. ^{31}P{^{1}H} NMR spectra of a newly prepared sample of [**2o**][SbF$_6$] in water (bottom) and after storage for up to 72 hours in water at 25 ˚C.

III. Peptide Synthesis and Protein Expression

The following general protocol was followed for all solid phase peptide syntheses:

Preparation of Resin:

Rink amide resin (1 g, 0.44 mmol/g) was weighed out and added to a 25 mL peptide synthesis vessel. Dimethylformamide (DMF; 10 mL) was added and the resin was shaken for a minimum of 1 h to swell. The resin was subsequently washed with DMF (3 × 10 mL), dichloromethane (3 × 10 mL), and DMF (3 × 10 mL).

First Deprotection:

A 20% solution of 4-methylpiperdine in DMF (10-15 mL/g of resin) was added and the vessel was shaken for 20 min. After shaking, the resin was washed once with DMF (10 mL). The 20% solution of 4-methylpiperdine in DMF (10-15 mL/g of resin) was added and the vessel was shaken for an additional 5 minutes. The resin was then washed three times with DMF (10 mL, 1 min washes) to ensure complete removal of 4-methylpiperdine.

Coupling of Amino Acids:

Amino acid (3 equiv to resin) and HBTU (2.9 equiv to resin) were weighed out and dissolved in DMF (10 mL). Once dissolved, DIPEA (6 equiv to resin) was added and the mixture stirred for 1 min. This mixture was then added to the resin and the resin was subjected to shaking for 45 min. After shaking, the resin was washed with DMF (3 × 10 mL, 1 min intervals) to ensure the complete removal of residual amino acid.

Coupling of Cysteine:

Coupling of Cysteine was performed using a procedure from: Han, Y. Albericio, F.; Barany, G. *J. Org. Chem.*, **1997**, *62*, 4307-4312.

Cysteine (3 equiv to resin), HATU (4 equiv to resin), and HOAt (0.6 M in DMF, 4 equiv to resin) were combined in DMF (6 mL) and CH_2Cl_2 (6 mL). Once dissolved, 2,4,6-trimethylpyridine (4 equiv to resin) was added and the mixture stirred quickly (1-2 seconds) and added to the resin. The mixture was shaken for 1 h. After shaking, the resin was washed with DMF (5 × 10 mL, 1 min intervals) to ensure the removal of residual amino acid. After the coupling of cysteine, the normal protocol was followed.

Deprotection of Amino Acids After Coupling:

A 20% solution of 4-methylpiperdine in DMF (10-15 mL/g of resin) was added and the vessel was shaken for 10 min. After shaking, the resin was washed once with DMF (10 mL). The 20% solution of 4-methylpiperdine in DMF (10-15 mL/g of resin) was added and the vessel was shaken for an additional 5 min. The resin was then washed three times with DMF (10 mL, 1 minute washes) to ensure the compete removal of 4-methylpiperdine.

Cleavage from Resin:

After the final deprotection, the resin was washed with DCM (3 × 10 mL). The dried resin was transferred to a 20 mL scintillation vial equipped with a magnetic stir bar and a septum. Argon gas was flowed over the resin for 5 minutes. A cleavage cocktail consisting of a 95:2.5:2.5 mixture of TFA:H_2O:TIPS (TIPS = triisopropylsilane) was prepared and added to the resin. The slurry was stirred for 3-4 hours under argon. Cleavage time depends on the amino acid composition of the peptide. Aliquots of the slurry were analyzed via LC-MS after filtration through a small pipette filter and dilution with water to determine full removal of peptide protecting groups. After 3-4 h, the cleavage cocktail was filtered and the filtrate was concentrated under a stream of argon until 1 mL remained. To this solution was added cold (-20 °C) diethyl ether, resulting in the precipitation of the crude peptide. The suspension was centrifuged, the supernatant was decanted. This washing process was repeated twice more, and then the resulting solids were dried under reduced pressure.

*It is important to use fresh TIPS solutions. TIPS stored longer than two months is less effective.

All peptides were stored in sealed containers under argon at -20 °C.

The isolated crude peptides were purified by reversed-phase HPLC (retention time 5.5-6.6 min using procedure described in SI section I). The obtained pure fractions were combined, and lyophilized.

Protein Expression

DARPin-Cys protein expression and purification was performed following literature procedures.[4]

DARPin-Cys Sequence (Calculated Mass: 13747.3 Da):

GGCGGSDLGKKLLEAARAGQDDEVRILMANGADVNAYDDNGVTPLHLAAFLGHLEI
VEVLLKYGADVNAADSWGTTPLHLAATWGHLEIVEVLLKHGADVNAQDKFGKTAF
DISIDNGNEDLAEILQKLN

FGF2 was expressed and purified from plasmid pET29c (+)hFGF-2, provided by Professor Thomas Scheper from the Helmholtz Centre for Infection Research (Braunschweig, Germany) according to Chen *et al.*[6]

FGF2 Sequence (Calculated Mass: 17122.6 Da):

AAGSITTLPALPEDGGSGAFPPGHFKDPKRLYCKNGGFFLRIHPDGRVDGVREKSDPHIK
LQLQAEERGVVSIKGVCANRYLAMKEDGRLLASKCVTDECFFFERLESNNYNTYRSRK
YTSWYVALKRTGQYKLGSKTGPGQKAILFLPMSAKS

Peptide Traces and Masses:

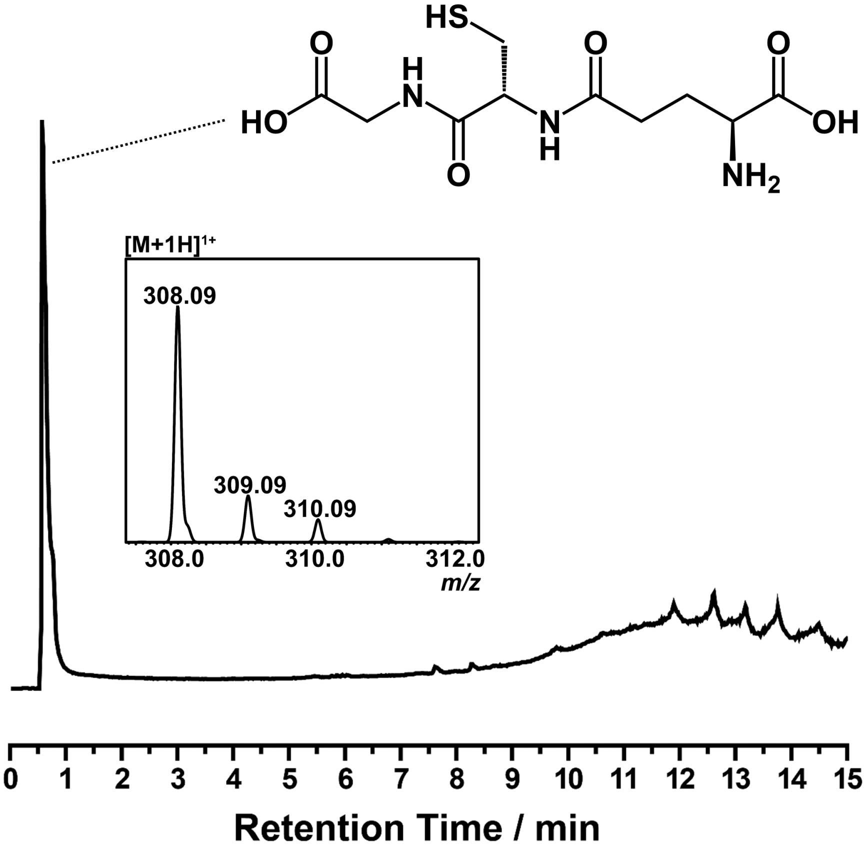


Figure S70. LC-MS trace for native GSH (BioXtra grade purchased from Sigma Aldrich). 308.0965 (calc'd 308.0911) *m/z* for $C_{10}H_{17}N_3O_6S$.

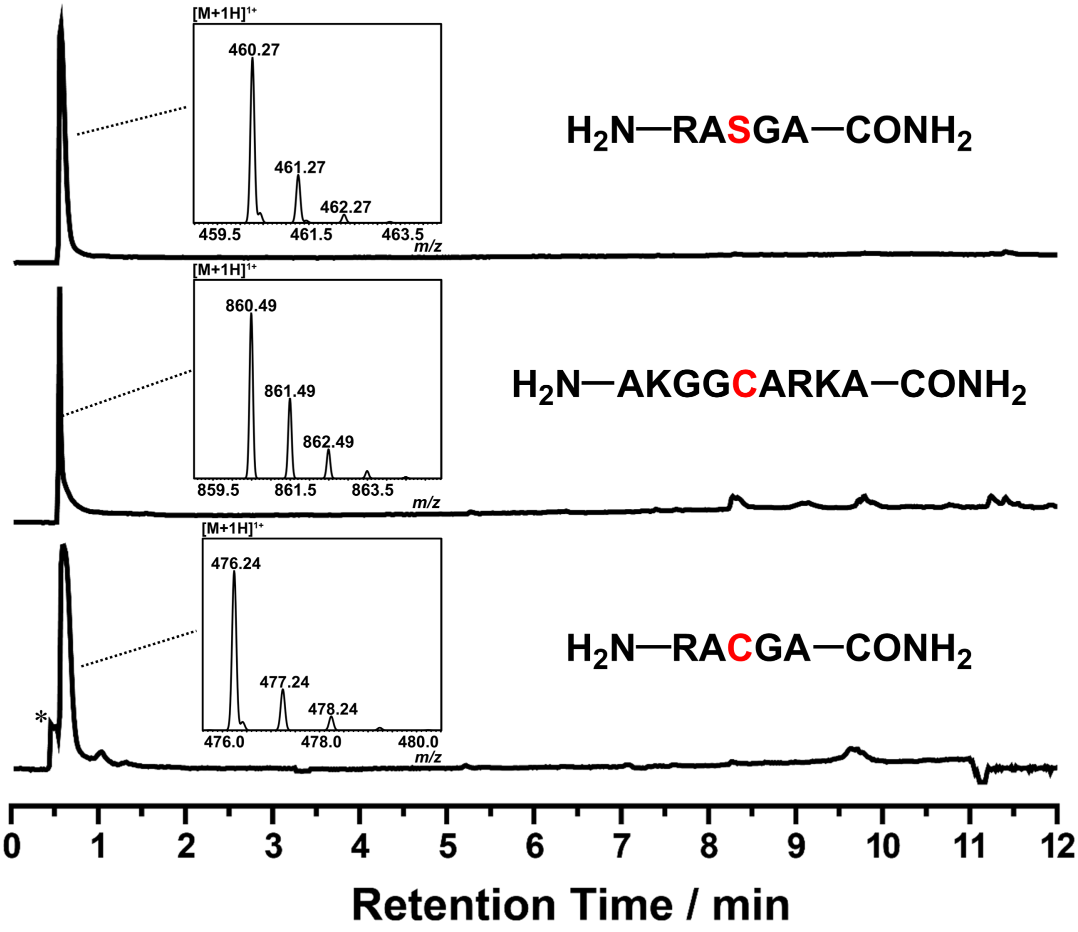


Figure S71. LC-MS traces for native peptides used in this study. (*) denotes Tris buffer (122 *m/z*). Top panel: 460.2605 (calc'd 460.2627) *m/z* for $C_{17}H_{33}N_9O_6$. Middle panel: 860.4908 (calc'd 860.4883) *m/z* for $C_{34}H_{65}N_{15}O_9S$. Bottom panel: 476.2416 (calc'd 476.2398) *m/z* for $C_{17}H_{33}N_9O_5S$.

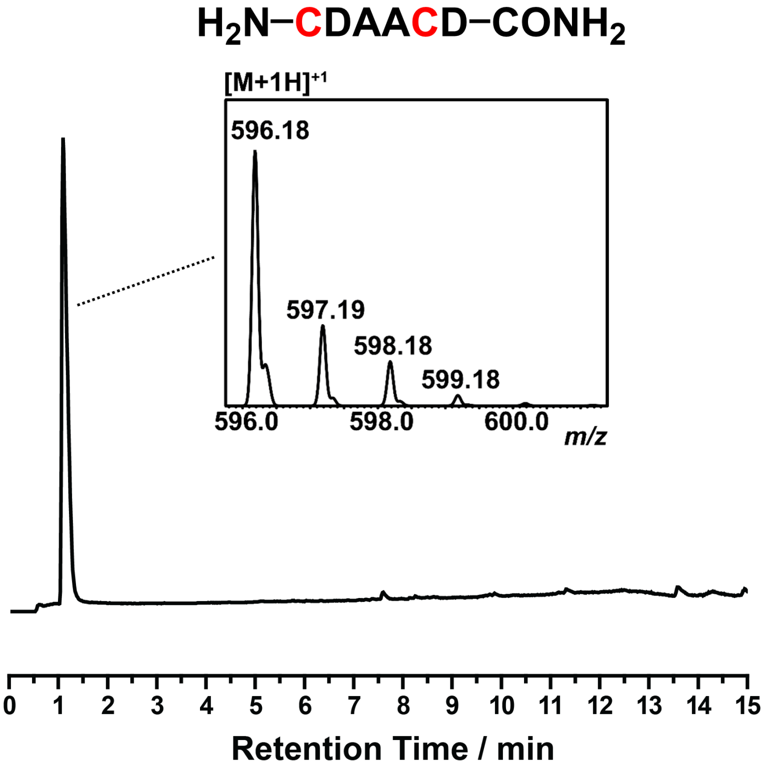


Figure S72. LC-MS trace for native dicysteine peptide. 596.1845 (calc'd 596.1803) *m/z* for $C_{20}H_{33}N_7O_{10}S_2$.

IV. Procedures and Characterization for Cysteine Arylation

Procedure and Characterization Data for Peptide Arylation Studies Using Complex [1][NTf$_2$].

After the oxidative addition reaction of 4-iodotoluene with (DPCb)AuNTf$_2$ proceeded to quantitative conversion (>99%) as determined by ^{31}P NMR analysis, the reaction mixture was filtered through Celite and dichloromethane was removed from the filtrate under reduced pressure to produce a yellow solid. A 15 mM stock solution was prepared by dissolution of the obtained yellow solids in MeCN.

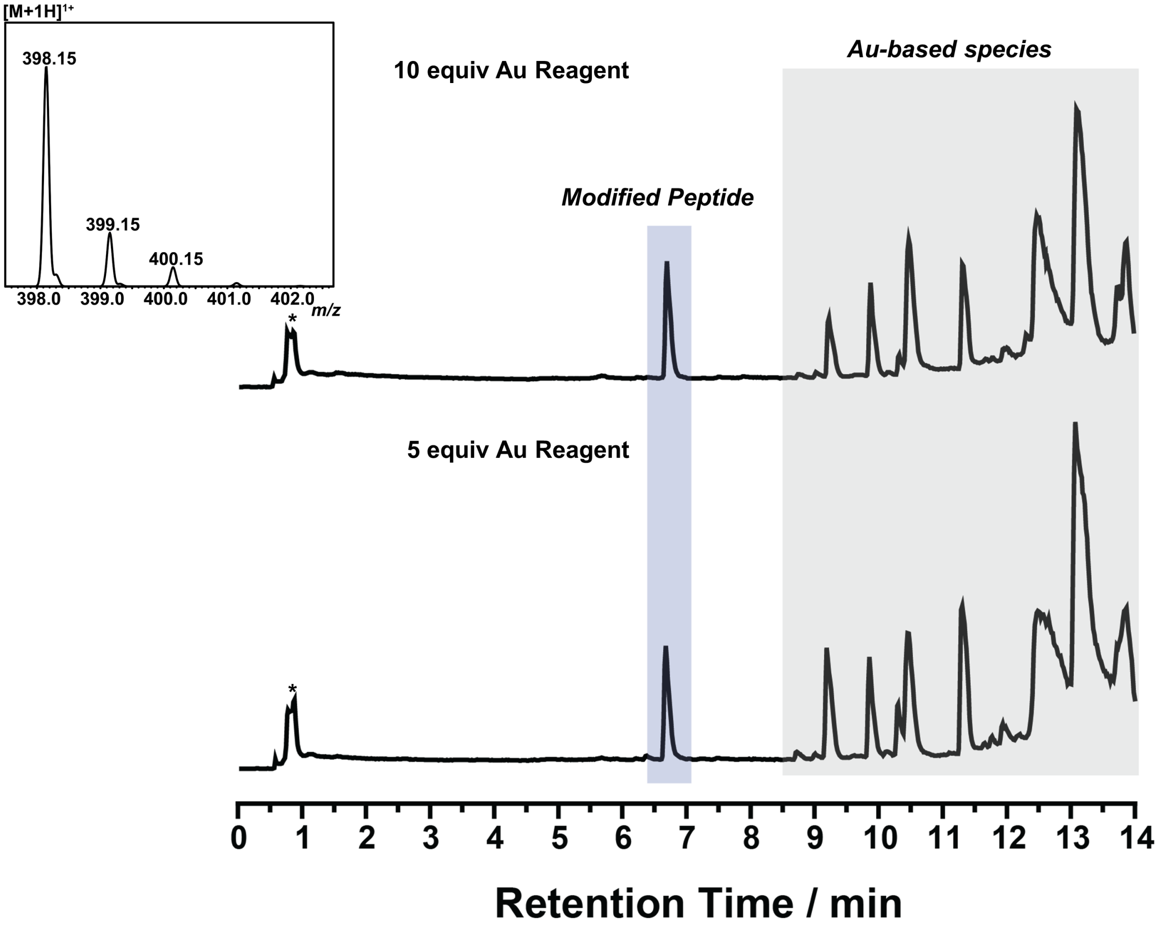


Figure S73. LC-MS traces for arylation of GSH using **1** at different reagent loadings. (*) denotes buffer. 398.1450 (calc'd 398.1380) *m/z* for $C_{17}H_{23}N_3O_6S$.

Procedure and Characterization Data for Water Equivalents Screen of Peptide Arylation Using [1][NTf$_2$].

After the oxidative addition reaction of 4-iodotoluene with (DPCb)AuNTf$_2$ proceeded to quantitative conversion (>99%), the solvent was removed under reduced pressure to produce a yellow solid. The yellow solid was dissolved in acetonitrile to prepare a 30 mM stock solution. Stock solutions of 15 mM and 10 mM were prepared from the initial 30 mM stock solution of the gold reagent in acetonitrile. A 2 mM solution of glutathione was prepared in 200 mM pH 8.0 Tris buffer. Reaction solutions were prepared in the following manner:

H_2O:MeCN	Gold Complex Stock Solution	Peptide Stock Solution	Water Added
90:10	10 µL of 30 mM	50 µL	40 µL
80:20	20 µL of 15 mM	50 µL	30 µL
70:30	30 µL of 10 mM	50 µL	20 µL

To a 2 mL Eppendorf tube was added 50 µL of the peptide stock solution and the appropriate amount of water (MilliQ). To this solution was added the appropriate amount of gold reagent stock solution, and the Eppendorf tube was vortexed (<5 seconds). After 1 min, a 20 µL aliquot was removed and diluted in a 100 µL solution of 1:1 H_2O:MeCN with 0.1% mol TFA. An aliquot from this solution was analyzed via LCMS.

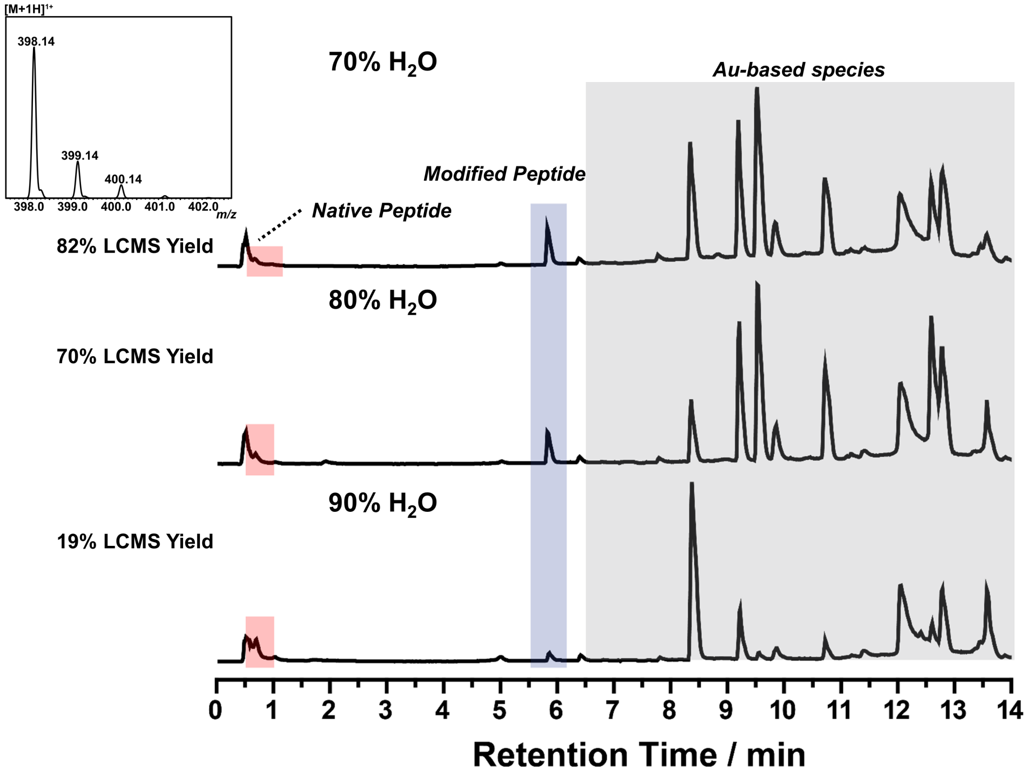


Figure S74. LC-MS traces for arylation of GSH using [**1**][NTf$_2$] in different water concentrations. 398.1433 (calc'd 398.1380) *m/z* for $C_{17}H_{23}N_3O_6S$.

Procedure and Characterization Data for Reagent Equivalents Screen of Peptide Arylation Using [2a][SbF_6].

Acetonitrile solutions of [**2a**][SbF_6] were prepared in 6, 4, and 2 mM concentrations. A 2 mM solution of glutathione was prepared in 200 mM pH 8.0 Tris buffer. In a 2 mL Eppendorf tube was added 20 µL of the peptide solution and 20 µL of the reagent solution, and the sample was then vortexed (<5 seconds). At one min, a 20 µL aliquot was removed from the reaction mixture and diluted in 100 µL of a solution of 1:1 H_2O:MeCN with 0.1% TFA. An aliquot from this solution was analyzed via LCMS.

Reagent:Peptide	Gold Complex Stock	Peptide Stock
3:1	20 µL of 6 mM	20 µL
2:1	20 µL of 4 mM	20 µL
1:1	20 µL of 2 mM	20 µL

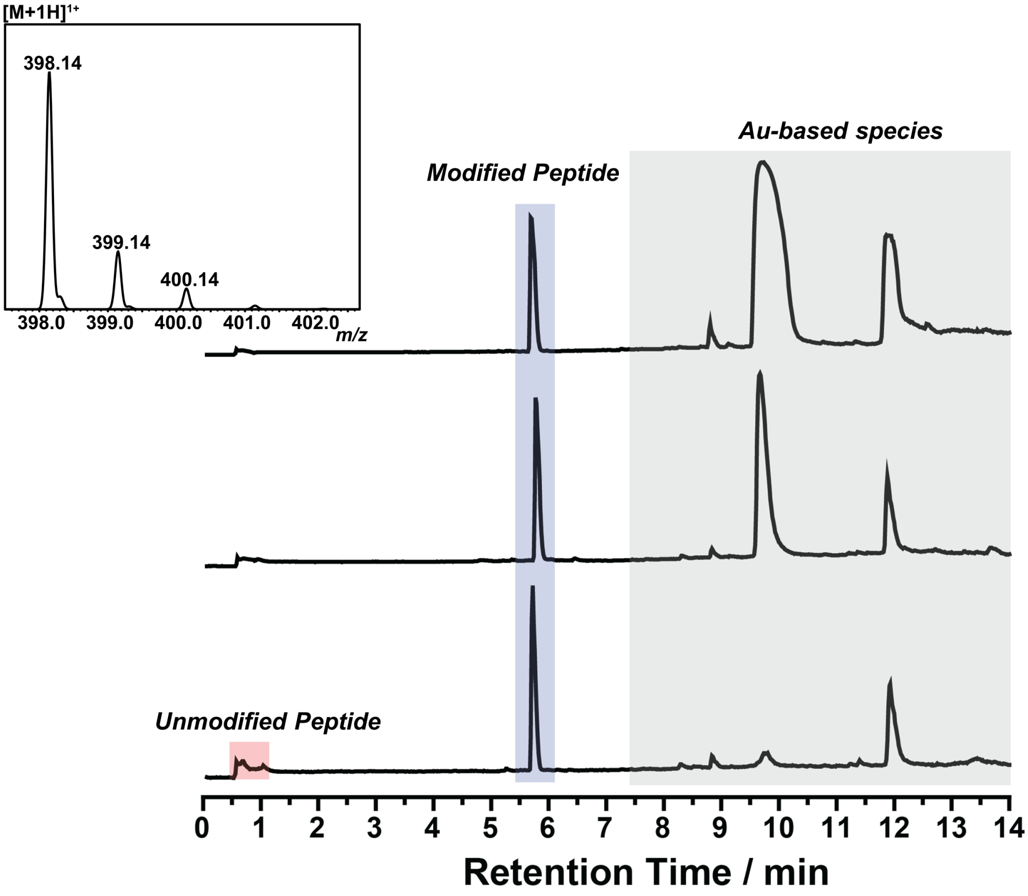


Figure S75. LC-MS traces for arylation of GSH using [**2a**][SbF_6] at different reagent loadings. 398.1417 (calc'd 398.1380) *m/z* for $C_{17}H_{23}N_3O_6S$.

Procedure and Characterization Data for Water Equivalents Screen of Peptide Arylation Using [2a][SbF_6]

Acetonitrile solutions of [**2a**][SbF_6] at 30, 15, and 10 mM concentrations were prepared. A 2 mM solution of glutathione was prepared in 200 mM pH 8.0 Tris buffer. Reaction solutions were prepared in the following manner:

H_2O:MeCN	Gold Complex Stock	Peptide Stock	Water Added
90:10	10 µL of 30 mM	50 µL	40 µL
80:20	20 µL of 15 mM	50 µL	30 µL
70:30	30 µL of 10 mM	50 µL	20 µL

To a 2 mL Eppendorf tube was added 50 µL of peptide stock solution and appropriate amount of water (MilliQ). To this solution was added the appropriate amount of gold reagent stock solution, and the Eppendorf tube was vortexed (<5 seconds). At one min, a 20 µL aliquot was removed and diluted in a 100 µL solution of 1:1 H_2O:MeCN with 0.1% mol TFA. An aliquot from this solution was analyzed *via* LCMS.

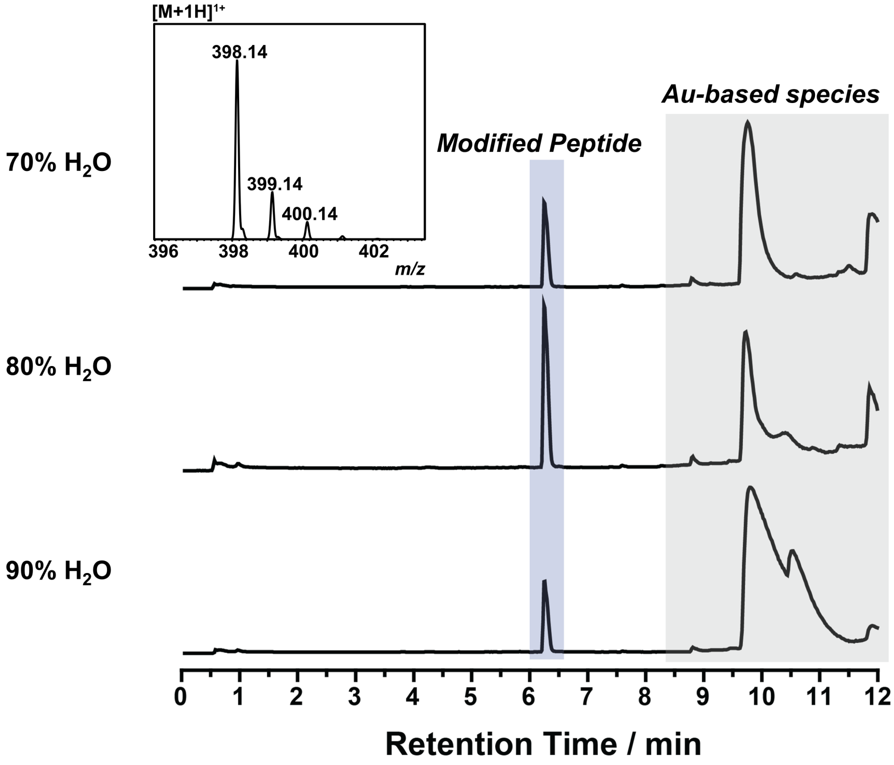
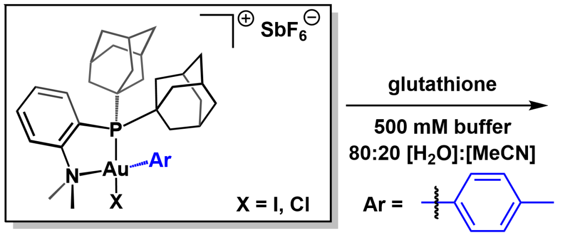


Figure S76. LC-MS traces for arylation of GSH using [**2a**][SbF_6] in different water concentrations. 398.1417 (calc'd 398.1380) *m/z* for $C_{17}H_{23}N_3O_6S$.

Procedure and Characterization Data for Buffer and pH Screen of Peptide Arylation Using [2a][SbF_6]

A 15 mM solution of [**2a**][SbF_6] in MeCN was prepared, and a 2 mM solution of glutathione was prepared in 1 M buffer.



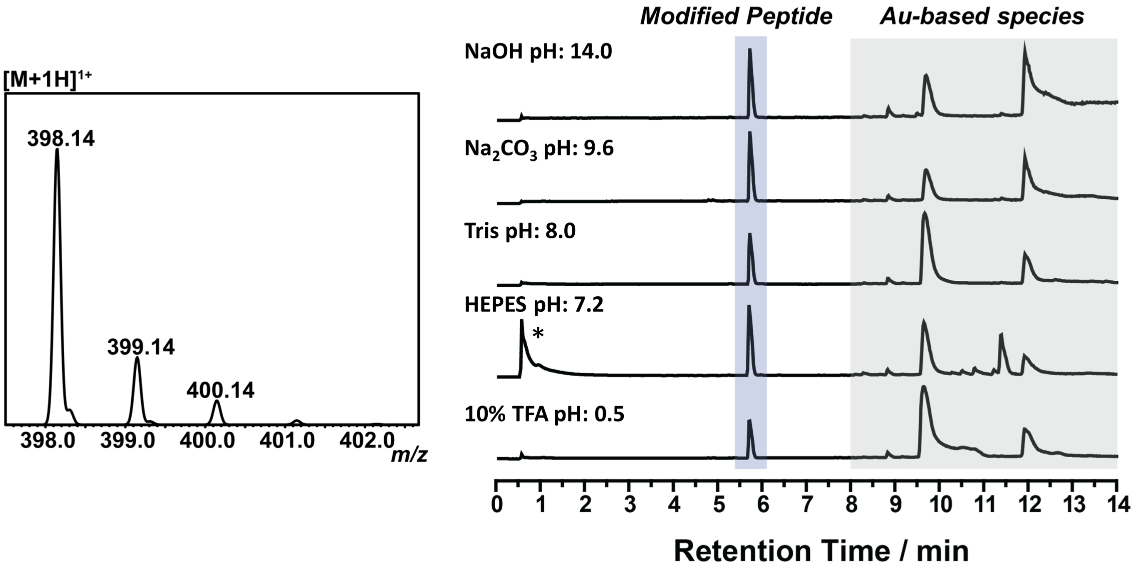


Figure S77. LC-MS traces for arylation of GSH using [**2a**][SbF_6] in different pH ranges. (*) denotes buffer. 398.1417 (calc'd 398.1380) *m/z* for $C_{17}H_{23}N_3O_6S$

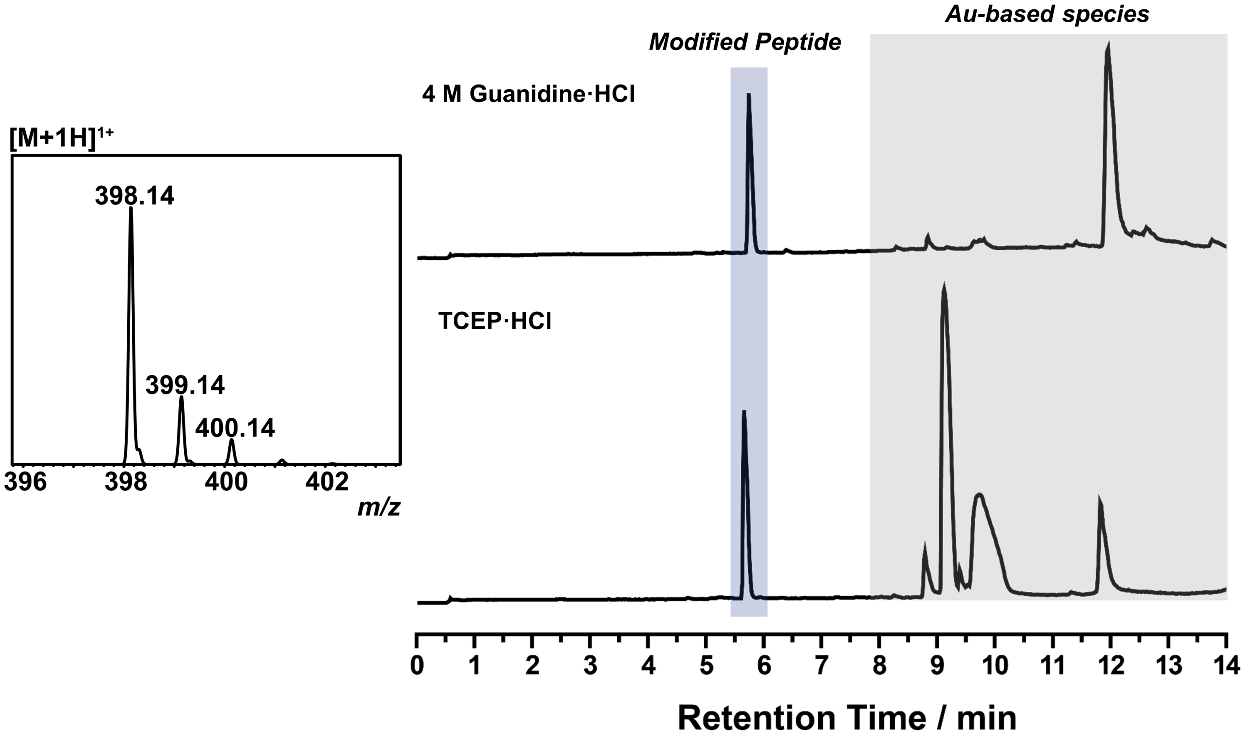


Figure S78. LC-MS traces for arylation of GSH using [**2a**][SbF$_6$] in the presence of 4 M guanidine·HCl (top) and TCEP·HCl. 398.1399 (calc'd 398.1380) *m/z* for $C_{17}H_{23}N_3O_6S$.

Cysteine Arylation in Unconventional Solvents

To a 2 mL Eppendorf tube was added 10 µL of peptide stock (20 mM) solution in 200 mM Tris pH 8.0 and 70 µL of solvent. To this solution was added 20 µL of the gold reagent stock solution (15 mM) in acetonitrile, and the Eppendorf tube was vortexed (<5 seconds). At one min, a 20 µL aliquot was removed and diluted in a 100 µL solution of 1:1 H_2O:MeCN with 0.1% mol TFA. An aliquot from this solution was analyzed *via* LCMS.

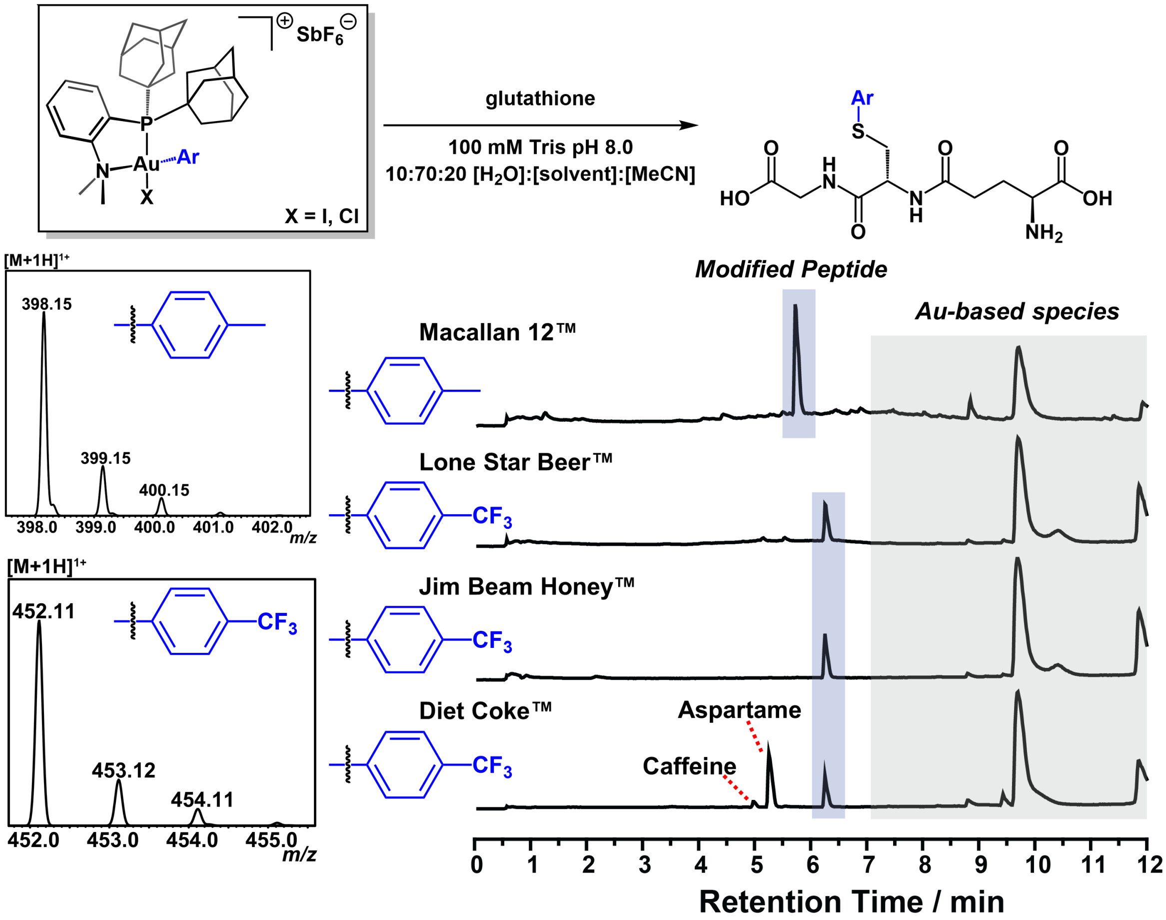
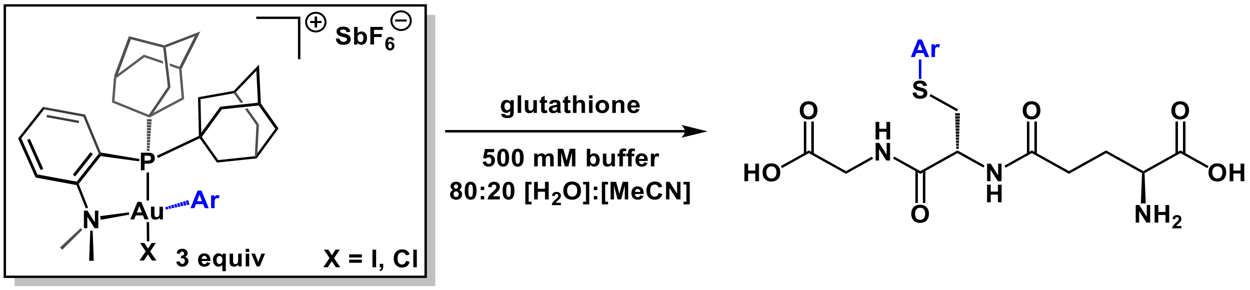


Figure S79. Arylation in unconventional solvents using [**2a**][SbF_6] and [**2b**][SbF_6]. ETolyl modified GSH: 398.1413 (calc'd 398.1380) *m/z* for $C_{17}H_{23}N_3O_6S$. *p*-CF_3 modified GSH: 452.1142 (calc'd 452.1098) *m/z* for $C_{17}H_{20}F_3N_3O_6S$.

Substrate Scope for Glutathione

To a 2 mL Eppendorf tube was added 50 µL of peptide stock solution in 1 M Tris pH 8.0 and 30 µL of water (MilliQ). To this solution was added 20 µL of a 15 mM gold reagent stock solution, and the Eppendorf tube was vortexed (<5 seconds). At one min, a 20 µL aliquot was removed and diluted in a 100 µL solution of 1:1 H_2O:MeCN with 0.1% mol TFA. An aliquot from this solution was analyzed *via* LCMS.



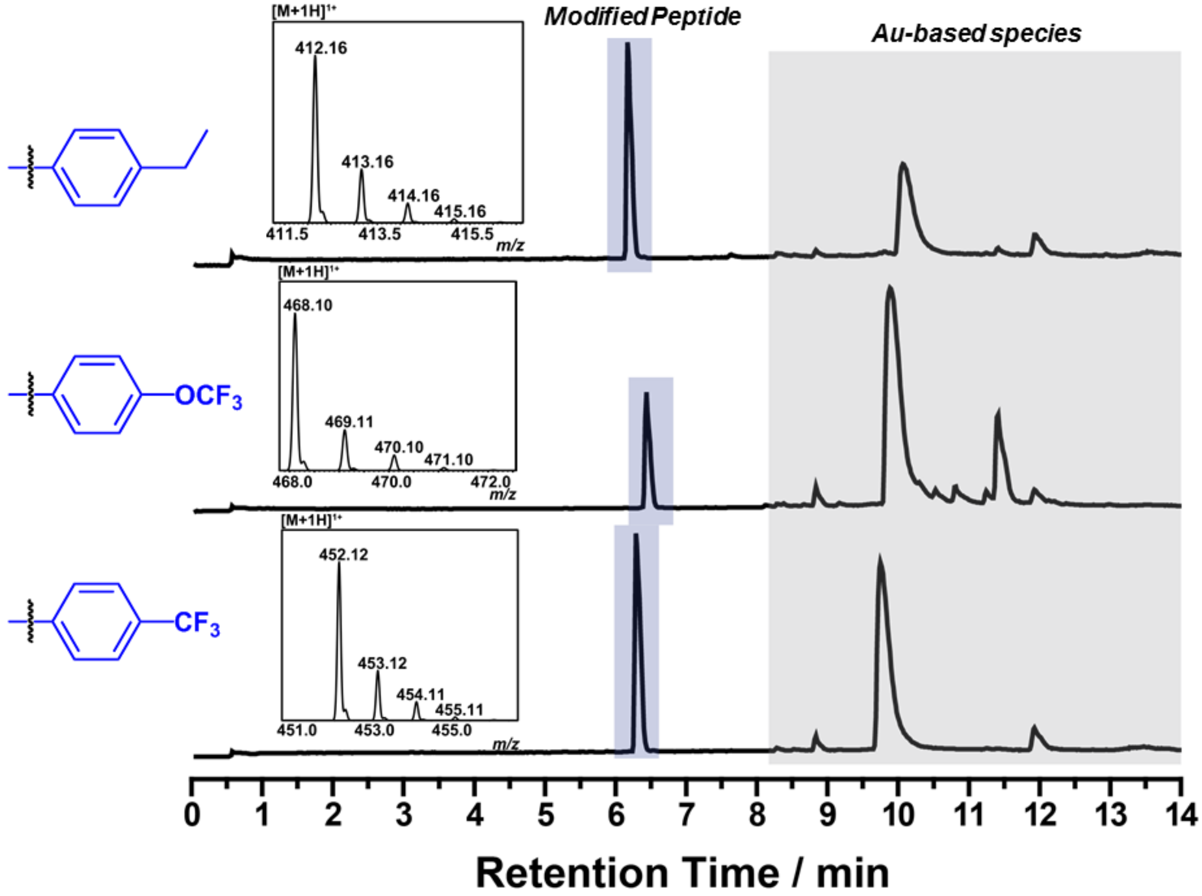


Figure S80. LC-MS traces for arylation of GSH using [**2b**][SbF_6], [**2g**][SbF_6], and [**2d**][SbF_6] with optimized conditions. Top panel: 412.1587 (calc'd 412.1537) *m/z* for $C_{18}H_{25}N_3O_6S$. Middle panel: 468.1099 (calc'd 468.1047) *m/z* for $C_{17}H_{20}F_3N_3O_7S$. Bottom panel: 452.1152 (calc'd 452.1098) *m/z* for $C_{17}H_{20}F_3N_3O_6S$.

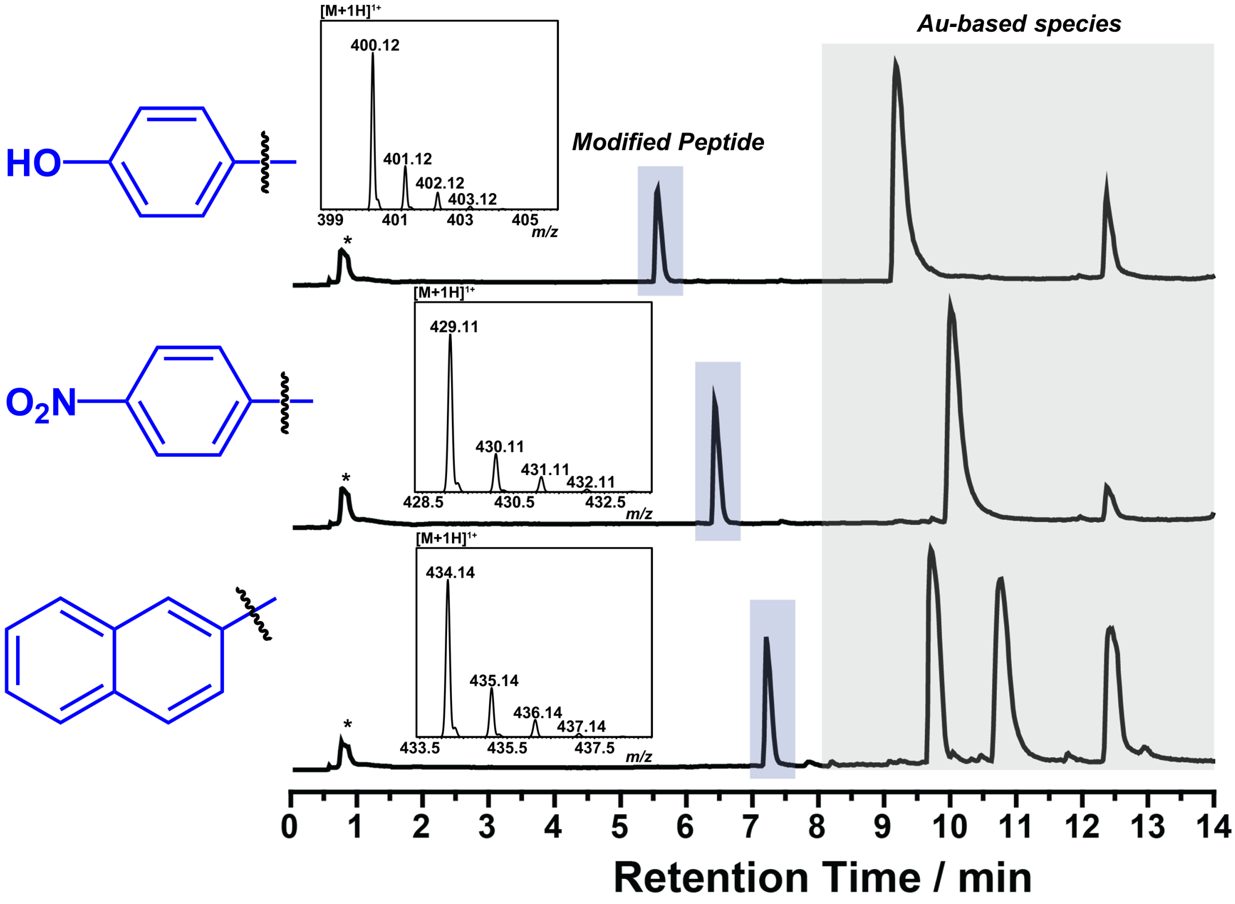


Figure S81. LC-MS traces for arylation of GSH using [**2f**][SbF_6]**,** [**2h**][SbF_6]**,** and [**2c**][SbF_6] with optimized conditions. (*) denotes Tris buffer (122 *m/z*). Top panel: 400.1200 (calc'd 400.1173) *m/z* for $C_{16}H_{21}N_3O_7S$. Middle panel: 429.1124 (calc'd 429.1075) *m/z* for $C_{16}H_{20}N_4O_8S$. Bottom panel: 434.1428 (calc'd 434.1380) *m/z* for $C_{20}H_{23}N_3O_6S$.

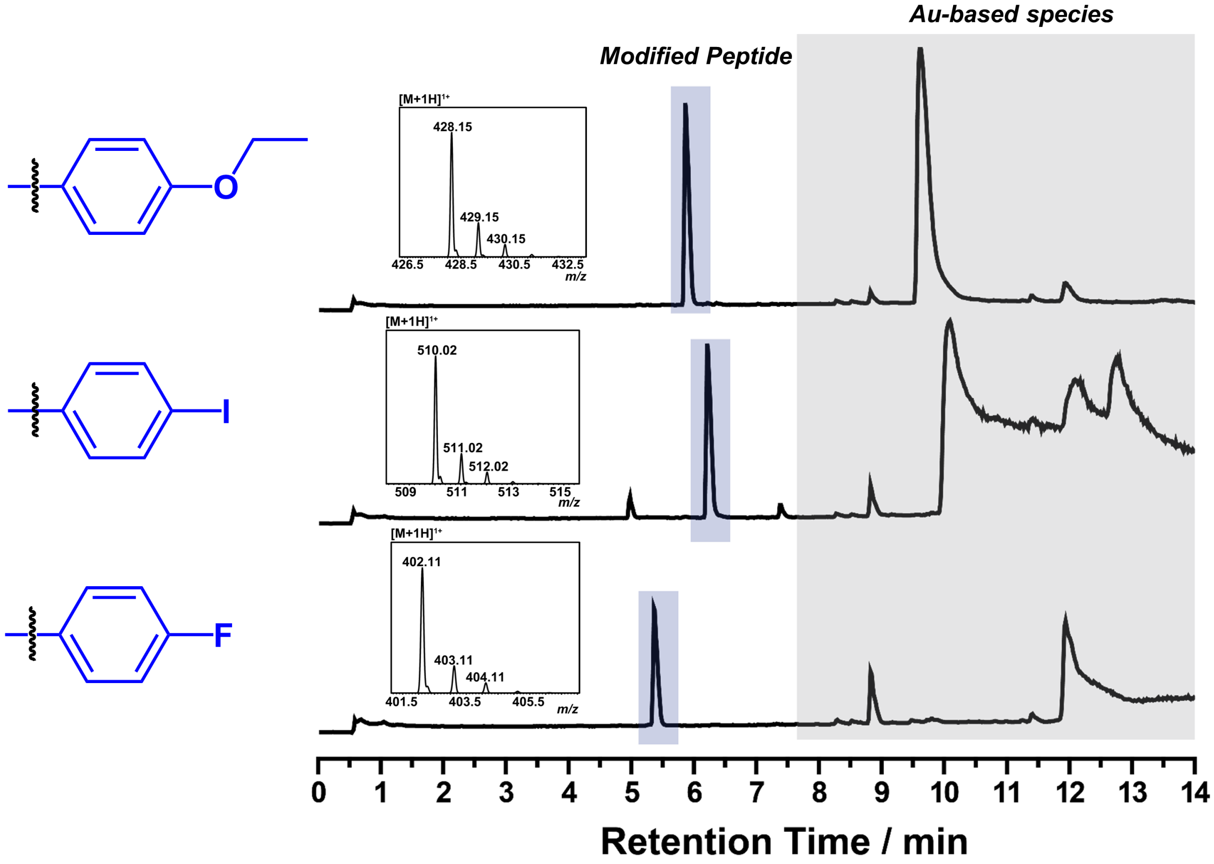


Figure S82. LC-MS traces for arylation of GSH using [**2e**][SbF_6], [**2k**][SbF_6], and [**2l**][SbF_6] with optimized conditions. Top panel: 428.1533 (calc'd 428.1486) *m/z* for $C_{18}H_{25}N_3O_7S$. Middle panel: 510.0217 (calc'd 510.0190) *m/z* for $C_{16}H_{20}N_3O_6IS$. Bottom panel: 402.1166 (calc'd 402.1130) *m/z* for $C_{16}H_{20}N_3O_6FS$.

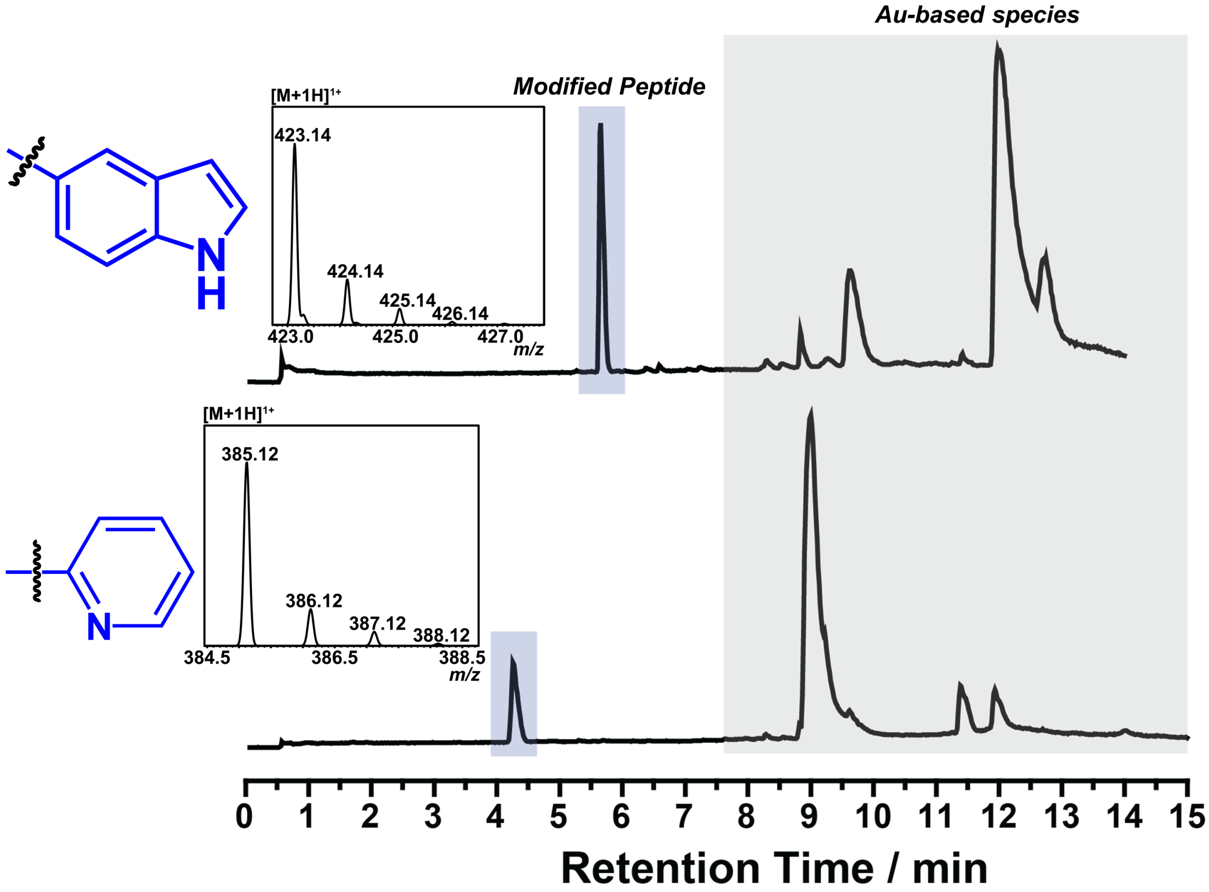


Figure S83. LC-MS traces for arylation of GSH using [**2p**][SbF$_6$] and [**2m**][SbF$_6$] with optimized conditions. Top panel: 423.1362 (calc'd 423.1333) *m/z* for $C_{18}H_{22}N_4O_6S$. Bottom panel: 385.1205 (calc'd 385.1176) *m/z* for $C_{15}H_{20}N_4O_6S$.

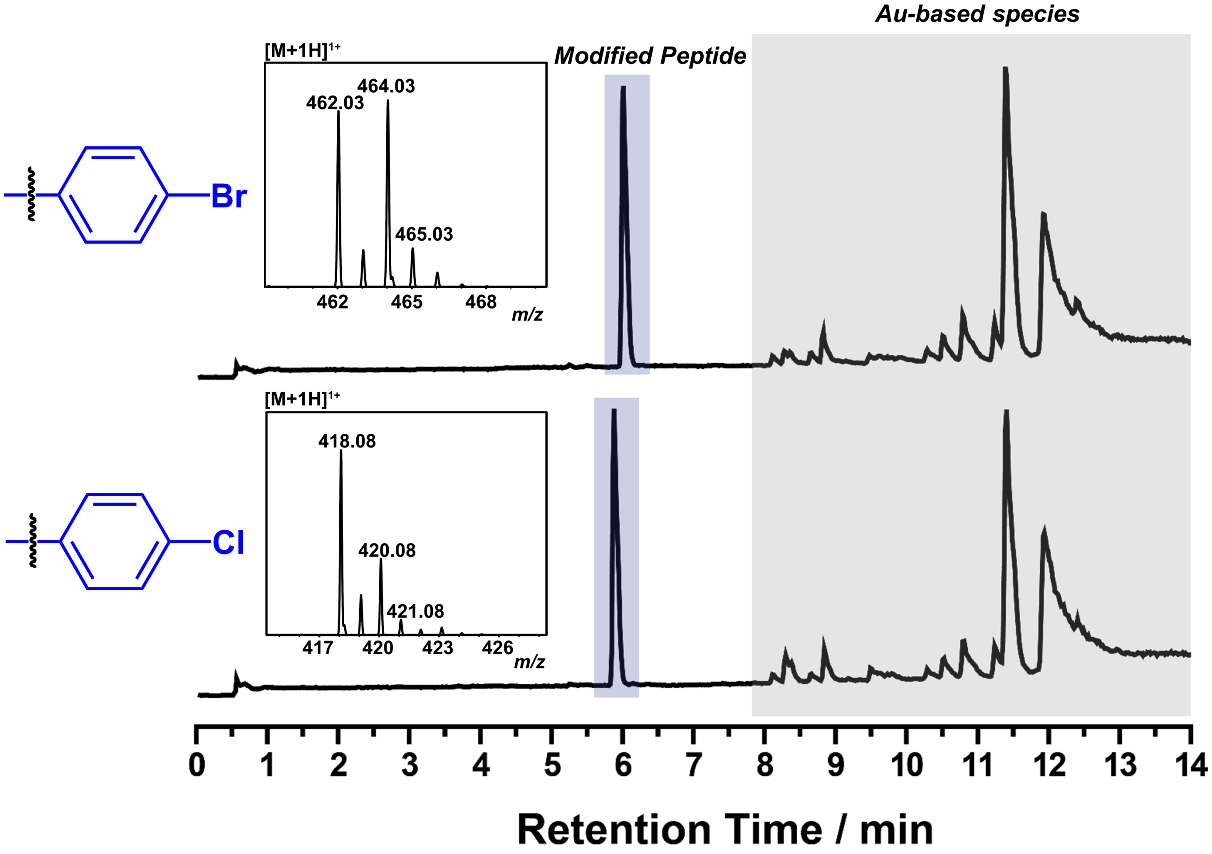


Figure S84. LC-MS traces for arylation of GSH using [**2j**][SbF$_6$] and [**2i**][SbF$_6$] with optimized conditions. Top panel: 462.0359 (calc'd 462.0329) *m/z* for $C_{16}H_{20}N_3O_6BrS$. Bottom panel: 418.0869 (calc'd 418.0834) *m/z* for $C_{16}H_{20}N_3O_6ClS$.

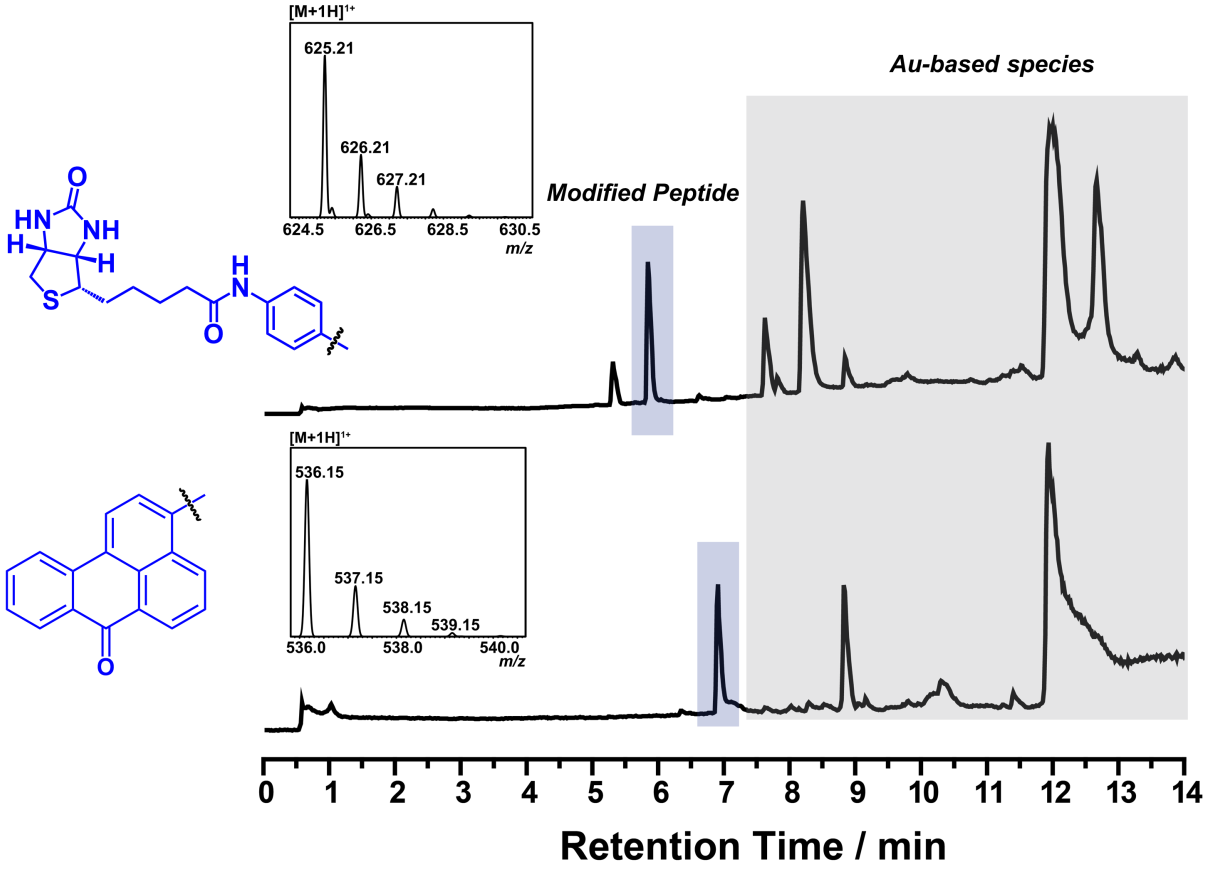


Figure S85. LC-MS traces for arylation of GSH using [**2q**][SbF_6] and [**2r**][SbF_6] with optimized conditions. Top panel: 625.2135 (calc'd 652.2109) *m/z* for $C_{26}H_{36}N_6O_8S_2$. Bottom panel: 536.1512 (calc'd 536.1486) *m/z* for $C_{27}H_{25}N_3O_7S$.

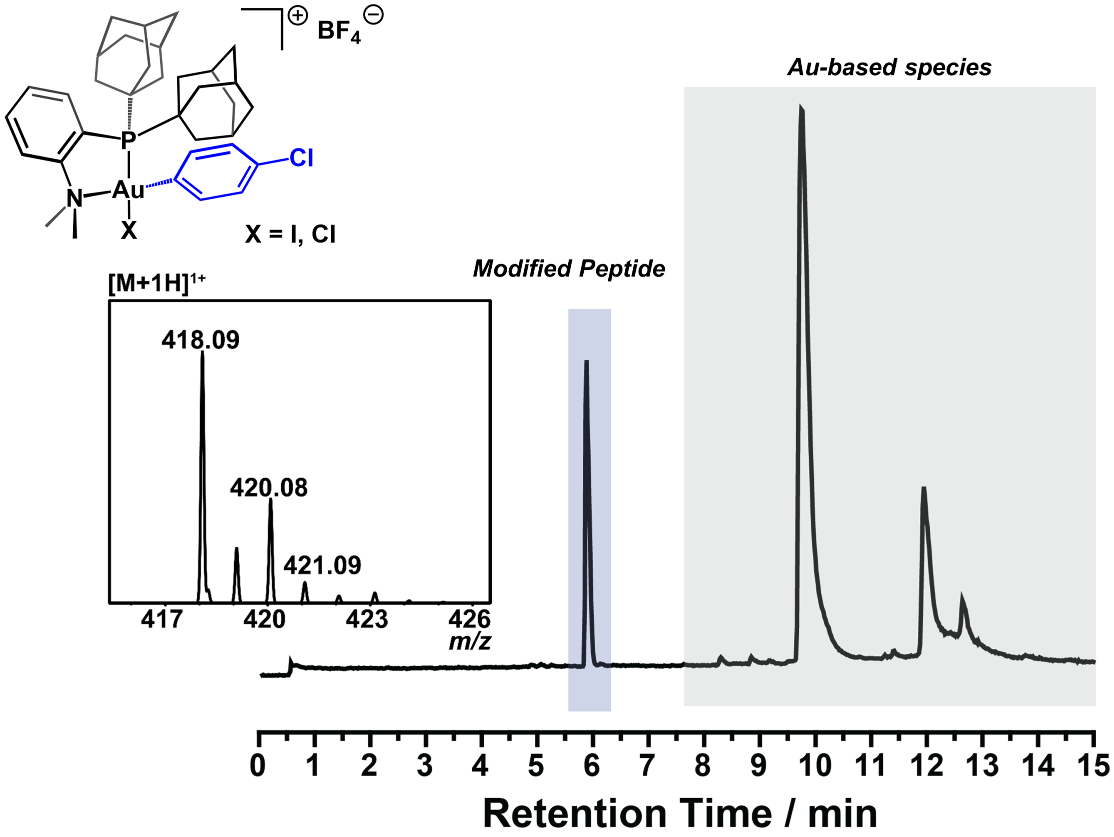


Figure S86. Modification of glutathione using [**2i**][BF_4] with optimized conditions. 418.0866 (calc'd 418.0834) *m/z* for $C_{16}H_{20}N_3O_6ClS$.

Au(III) and Pd(II) Competition Experiments with GSH

To 50 µL of a 2 mM GSH solution in 100 mM Tris buffer (pH 8.0) was added 20 µL of water followed by 45 µL of a mixture of [**2b**][SbF_6] (15 µL of a 10 mM MeCN solution) and (RuPhos)Pd(tolyl)I (30 µL of a 20 mM MeCN solution) in MeCN. The reaction mixture was vortexed for ca. 10 sec, and then allowed to stand at room temperature for 5 min. A 20 µL aliquot from the mixture was then diluted with a solution of thiopropionic acid (10 µL of a 0.3 M solution in H_2O) in a 1:1 H_2O:MeCN mixture with 0.1% TFA. An aliquot from this solution was analyzed by LCMS.

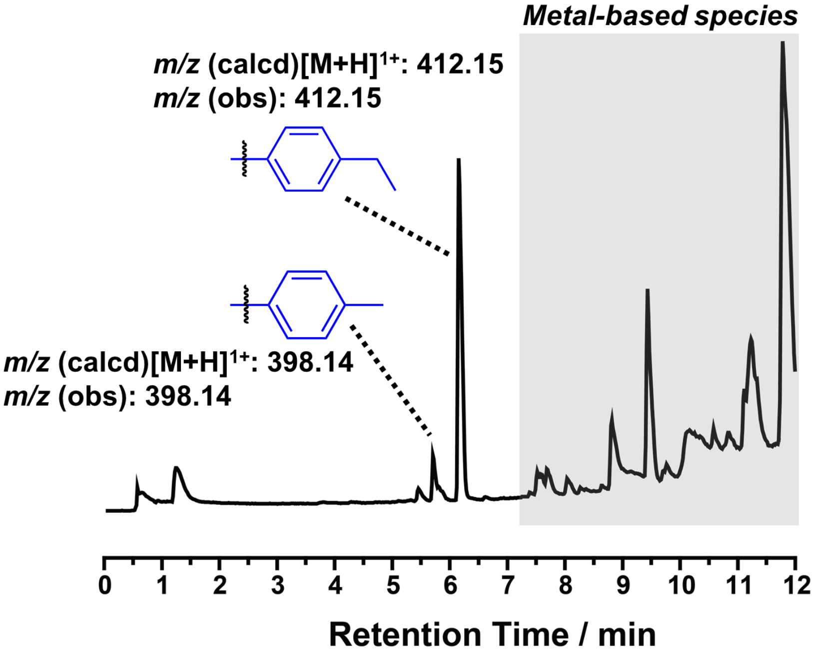


Figure S87. Representative LCMS trace for Au(III) and Pd(II) competition experiments. Ethylbenzene modified GSH: 412.1577 (calc'd 412.1537) *m/z* for $C_{18}H_{25}N_3O_6S$. Tolyl modified GSH: 398.1401 (calc'd 398.1380) *m/z* for $C_{17}H_{23}N_3O_6S$.

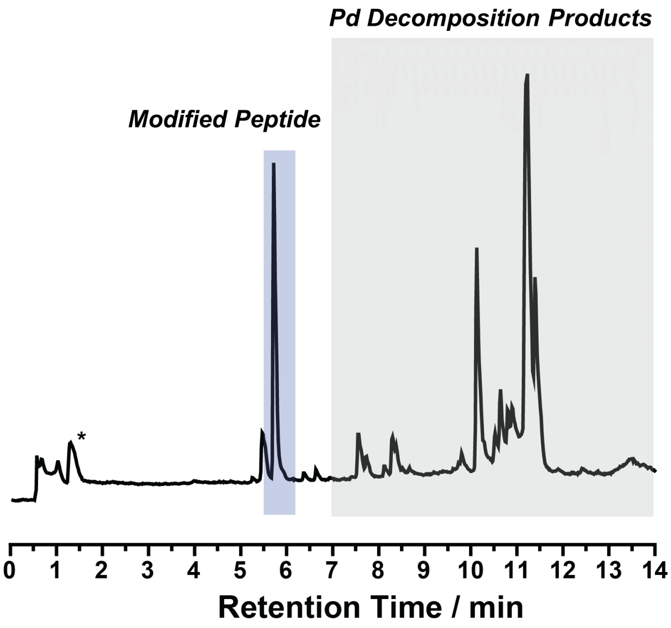
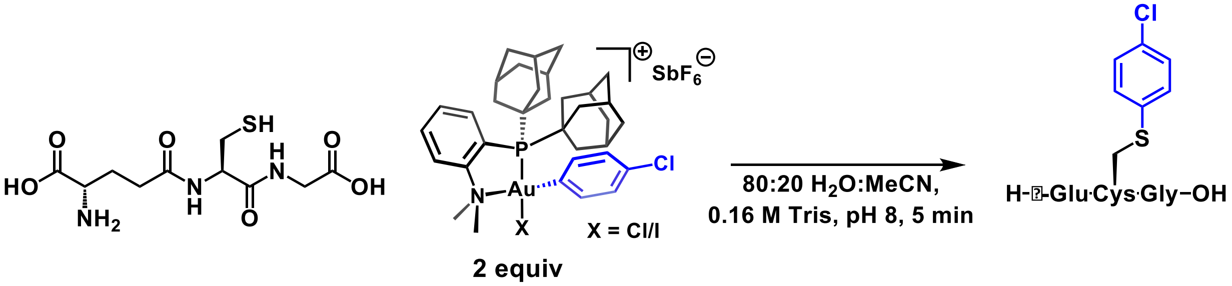


Figure S88. Modification of GSH using (RuPhos)Pd(tolyl)I in conditions replicating those used in Scheme 2 of the main text (100 mM Tris pH 8.0, 6:4 [H_2O]:[MeCN]).

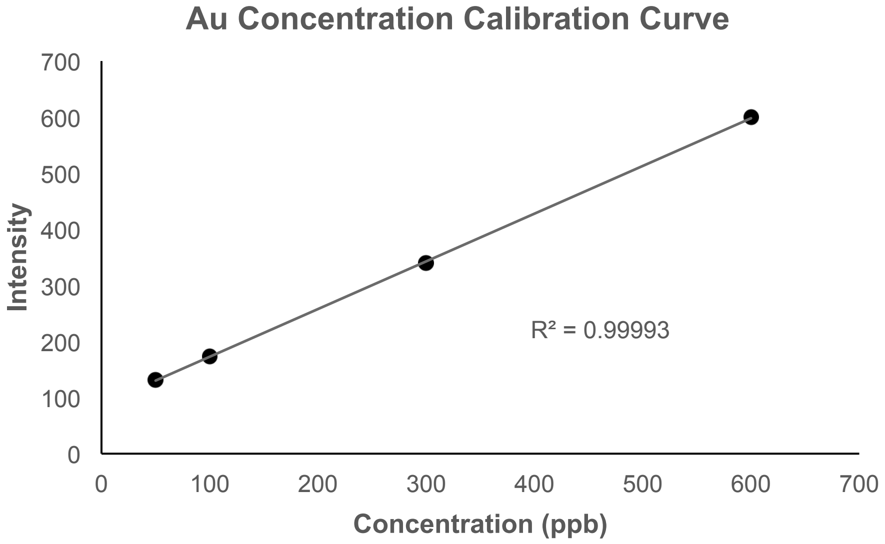
Preparation of *S*-(*p*-Cl-C_6H_4) GSH conjugate



To a solution of GSH (16 mg, 0.052 mmol, 1.0 equiv) in H_2O (8 mL, 0.2 M Tris, pH 8) was added a suspension of [**2i**][SbF_6] (116 mg, 0.116 mmol, 2.23 equiv) in MeCN (2 mL). The resulting suspension was sonicated for 30 sec, and then allowed to stand at 25 °C for an additional 4.5 min. The reaction mixture was then diluted with a 50/50 mixture of MeCN/H_2O containing 0.1%TFA, and the resulting suspension was centrifuged for 2 min, at which point the supernatant was decanted and passed through a 0.45 µm filter. The filtrate was lyophilized and the obtained solid was dissolved in H_2O containing 0.1% TFA and purified by semi-preparative reversed-phase HPLC.

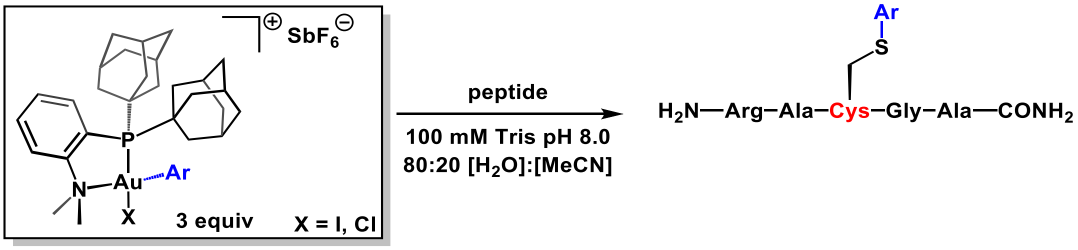
Solvent compositions for reversed-phase HPLC purification were: H_2O with 0.1% TFA (solvent A), MeCN with 0.1% TFA (solvent B). 0-5 min, 100% A; 5-60 min, linear gradient 100-60% A; 65-75 min, linear gradient 40-100% B. Flow rate: 3 mL/min. HPLC fractions containing the pure product were further confirmed by LC-MS, combined, and lyophilized.

ICP-AES was used to measure the remaining gold content in the purified *S*-(*p*-Cl-C_6H_4) GSH conjugate. Of the isolated material, 3.85 mg was dissolved in 10 mL of a 2% HCl (aq) solution (385 ppm concentration), and the material was filtered through a 0.45 µm filter. The resulting solution was analyzed by ICP-AES, and the concentration of gold in this sample was determined to be 55 ppb. This analysis indicates >99.9% efficiency for the removal of gold-containing species by the described purification procedure.



Substrate Scope for Larger Peptide Sequences

To a 2 mL Eppendorf tube was added 50 μL of peptide stock solution in 200 mM Tris pH 8.0 and 30 μL of water (MilliQ). To this solution was added 20 μL of a 15 mM gold reagent stock solution, and the Eppendorf tube was vortexed (<5 seconds). At one min, a 20 μL aliquot was removed and diluted in a 100 μL solution of 1:1 H_2O:MeCN with 0.1% mol TFA. An aliquot from this solution was analyzed *via* LCMS.



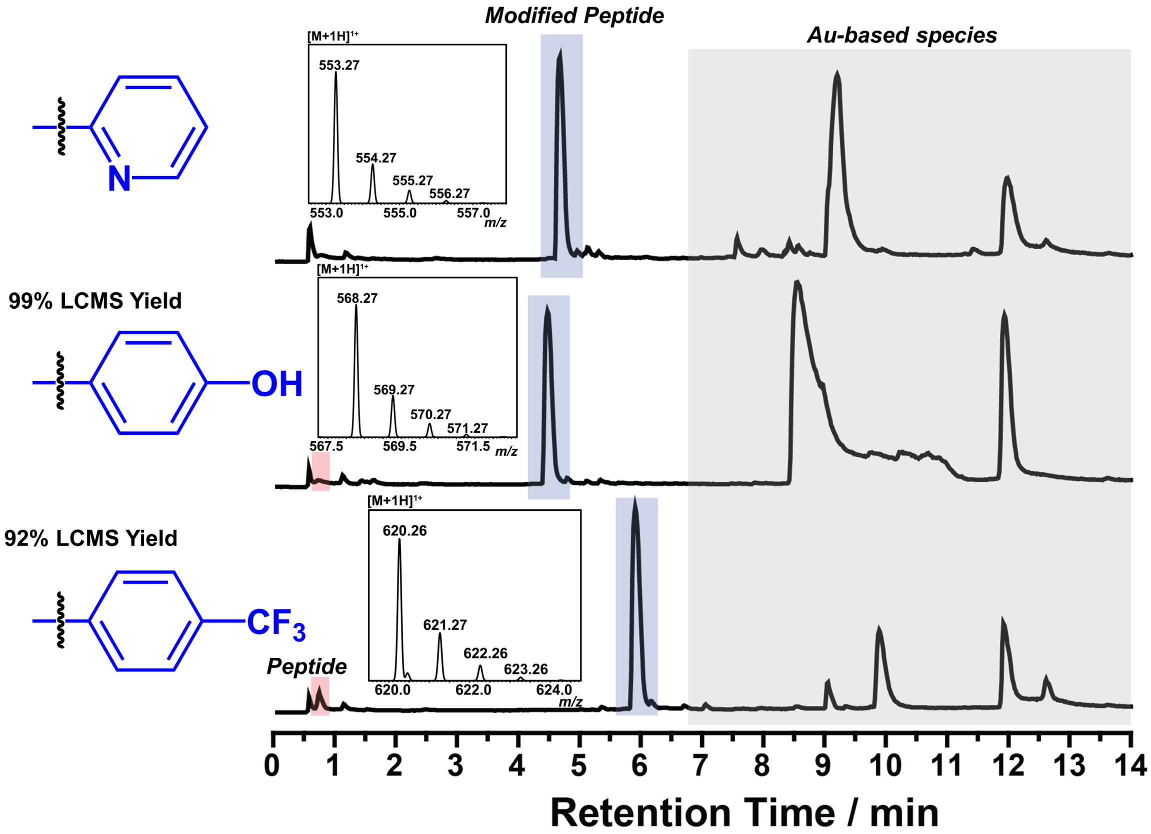


Figure S89. LC-MS traces for arylation of unprotected peptide using [**2m**][SbF_6], [**2f**][SbF_6], and [**2d**][SbF_6] with optimized conditions. Top panel: 553.2710 (calc'd 553.2664) *m/z* for $C_{22}H_{36}N_{10}O_5S$. Middle panel: 568.2700 (calc'd 568.2660) *m/z* for $C_{23}H_{37}N_9O_6S$. Bottom panel: 620.2639 (calc'd 620.2585) *m/z* for $C_{24}H_{36}F_3N_9O_5S$.

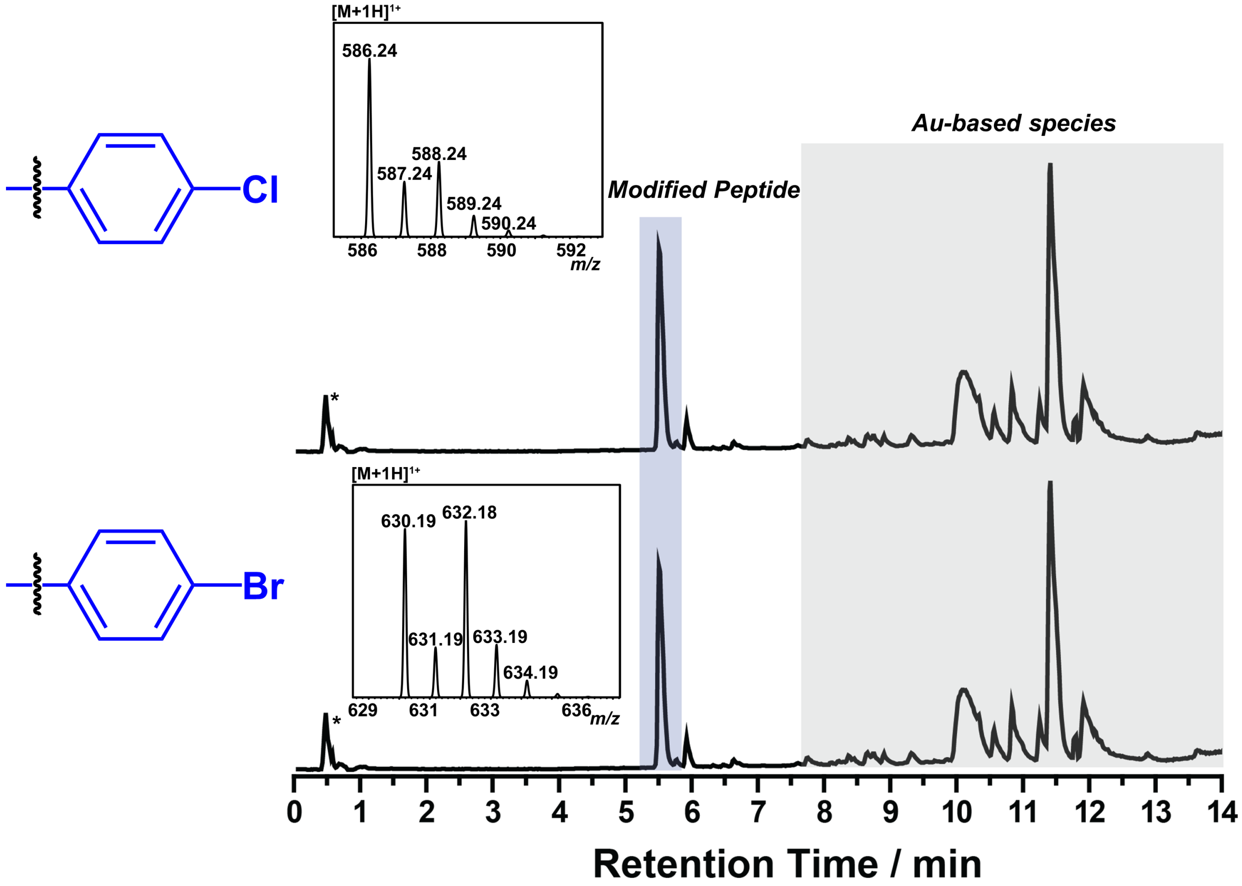


Figure S90. LC-MS traces for arylation of unprotected peptide using [**2i**][SbF$_6$] and [**2j**][SbF$_6$] with optimized conditions. (*) denotes Tris buffer (122 *m/z*). Top panel: 586.2371 (calc'd 586.2321) *m/z* for $C_{23}H_{36}ClN_9O_5S$. Bottom panel: 630.1864 (calc'd 630.1816) *m/z* for $C_{23}H_{36}BrN_9O_5S$.

To a 2 mL Eppendorf tube was added 50 µL of peptide stock solution in 1 M Tris pH 8.0. To this solution was added 50 µL of a 6 mM gold reagent stock solution, and the Eppendorf tube was vortexed (<5 seconds). At one min, a 20 µL aliquot was removed and diluted in a 100 µL solution of 1:1 H_2O:MeCN with 0.1% mol TFA. An aliquot from this solution was analyzed *via* LCMS.

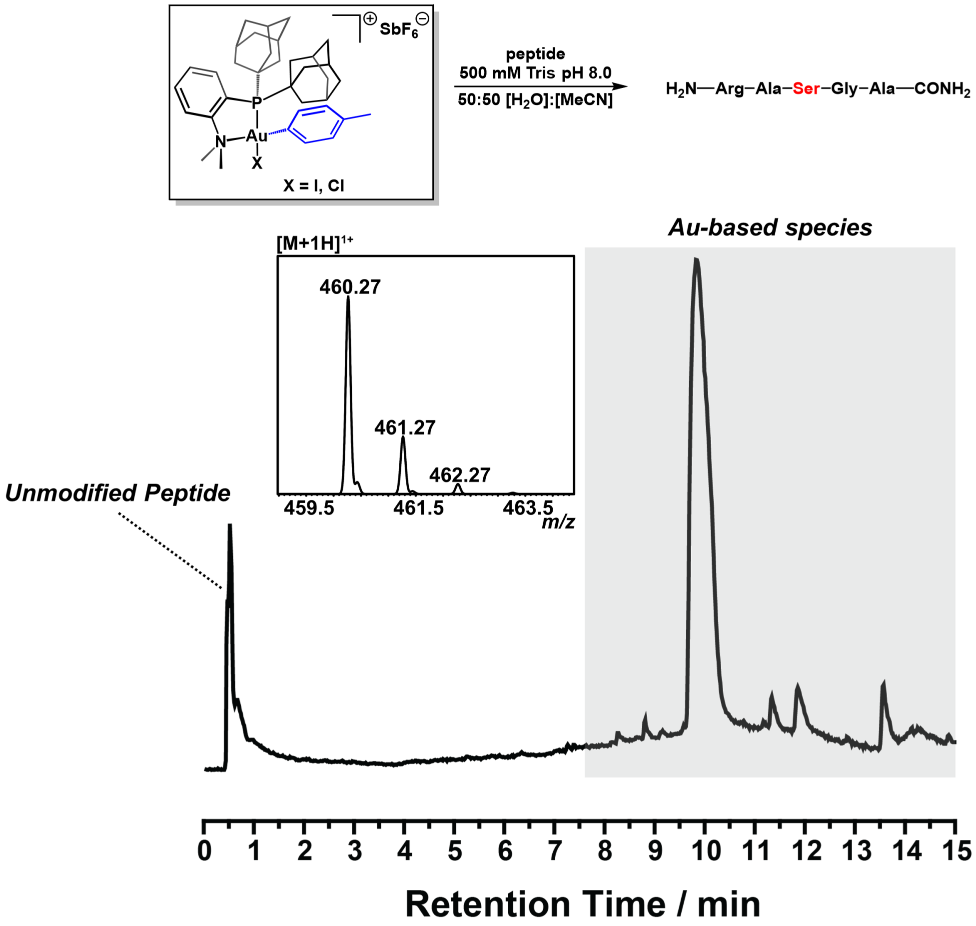
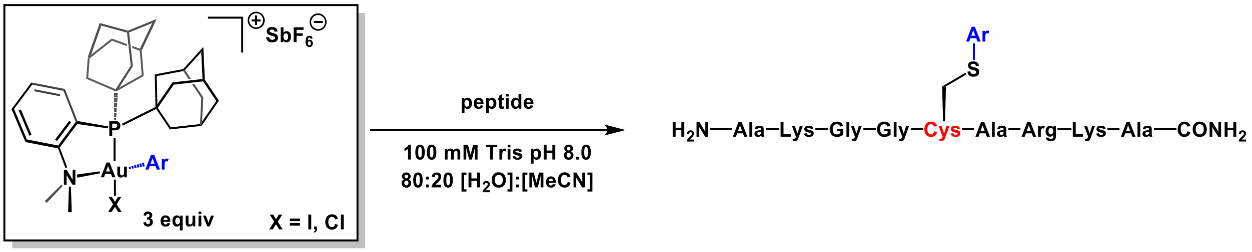


Figure S91. LC-MS trace of control reaction using serine substituted peptide. 460.2596 (calc'd 460.2627) *m/z* for $C_{17}H_{33}N_9O_6$.

To a 2 mL Eppendorf tube was added 50 μL of peptide stock solution in 200 mM Tris pH 8.0 and 30 μL of water (MilliQ). To this solution was added 20 μL of a 15 mM gold reagent stock solution in acetonitrile, and the Eppendorf tube was vortexed (<5 seconds). At one min, a 20 μL aliquot was removed and diluted in a 100 μL solution of 1:1 H_2O:MeCN with 0.1% mol TFA. An aliquot from this solution was analyzed *via* LCMS.



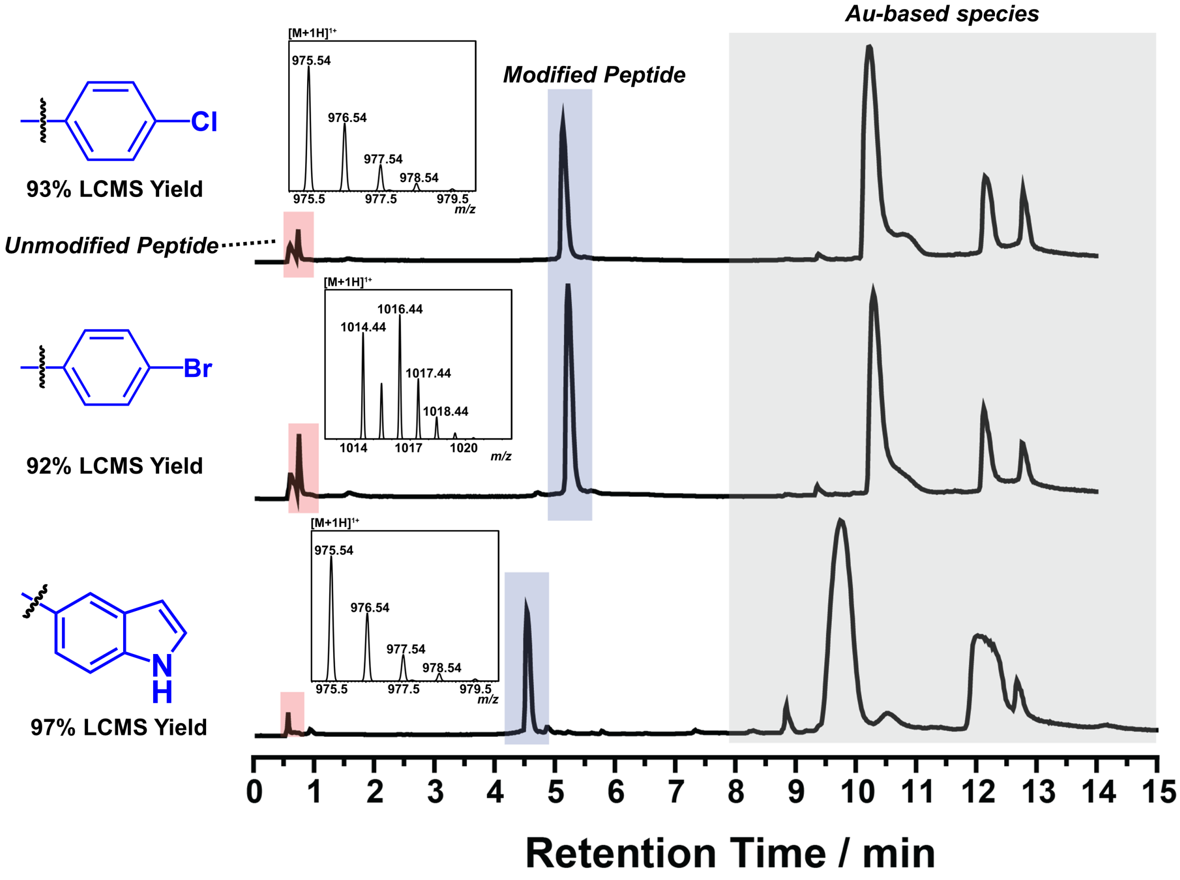


Figure S92. LC-MS traces for arylation of unprotected peptide using [**2i**][SbF_6], [**2j**][SbF_6], and [**2p**][SbF_6] with optimized conditions. Top panel: 970.4885 (calc'd 970.4806) *m/z* for $C_{40}H_{68}ClN_{15}O_9S$. Middle panel: 1014.4373 (calc'd 1014.4301) *m/z* for $C_{40}H_{68}BrN_{15}O_9S$. Bottom panel: 975.5369 (calc'd 975.5305) *m/z* for $C_{42}H_{70}N_{16}O_9S$.

Cysteine arylation using compound **2o**: To a 2 mL Eppendorf tube was added 50 µL of peptide stock solution in 200 mM Tris pH 8.0. To this solution was added 50 µL of a 6 mM gold reagent stock solution in water (MilliQ), and the Eppendorf tube was vortexed (<5 seconds). At one min, a 20 µL aliquot was removed and diluted in a 100 µL solution of 1:1 H_2O:MeCN with 0.1% mol TFA. An aliquot from this solution was analyzed *via* LCMS. Cysteine arylation using compound **2q** To a 2 mL Eppendorf tube was added 50 µL of peptide stock solution in 200 mM Tris pH 8.0 and 20 µL of water (MilliQ). To this solution was added 30 µL of a 10 mM gold reagent stock solution in acetonitrile, and the Eppendorf tube was vortexed (<5 seconds). At one min, a 20 µL aliquot was removed and diluted in a 100 µL solution of 1:1 H_2O:MeCN with 0.1% mol TFA. An aliquot from this solution was analyzed *via* LCMS.

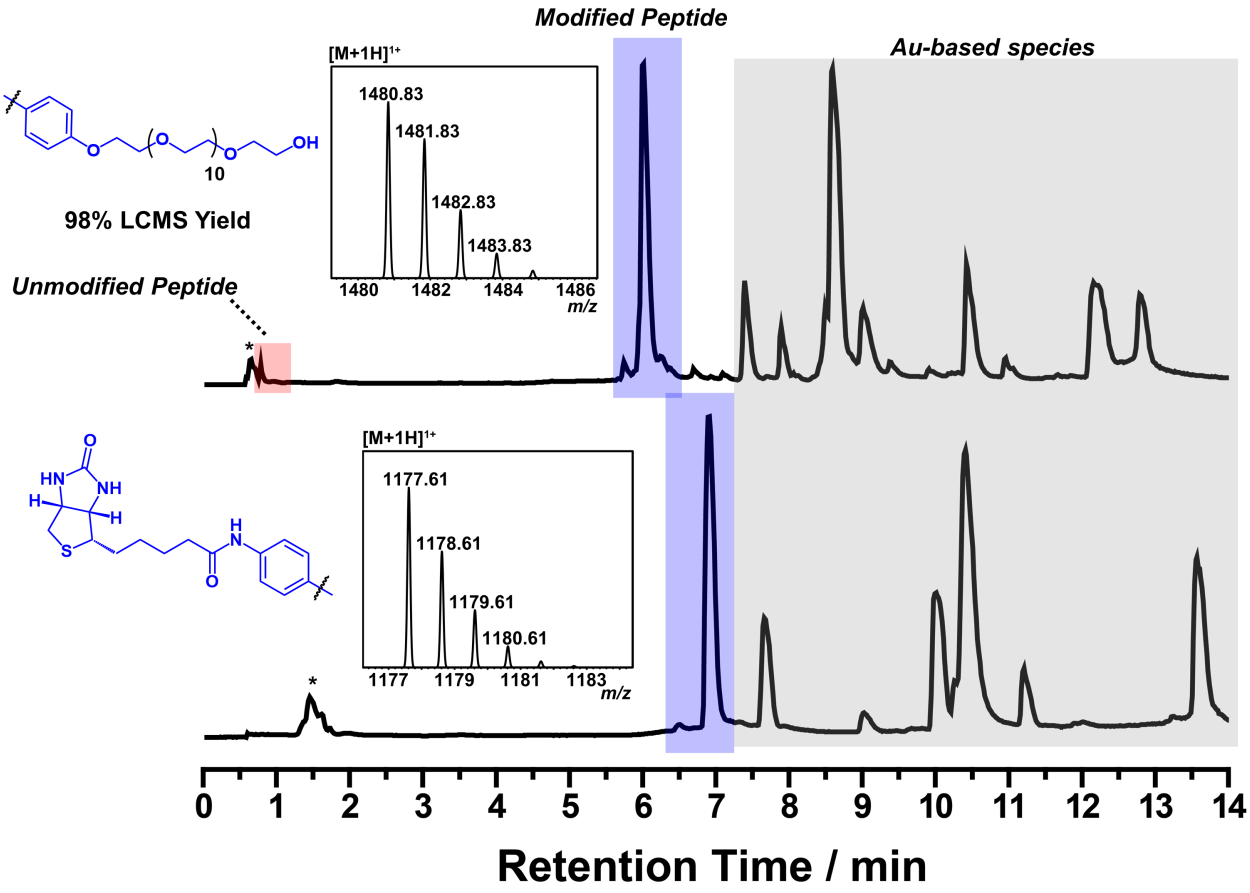


Figure S93. LC-MS traces for arylation of unprotected peptide using [**2o**][SbF_6] and [**2q**][SbF_6] with optimized conditions. (*) denotes Tris buffer (122 *m/z*). Top panel: 1480.8350 (calc'd 1480.8291) *m/z* for $C_{64}H_{117}N_{15}O_{22}S$. Bottom panel: 1177.6129 (calc'd 1177.6081) *m/z* for $C_{50}H_{84}N_{18}O_{11}S_2$.

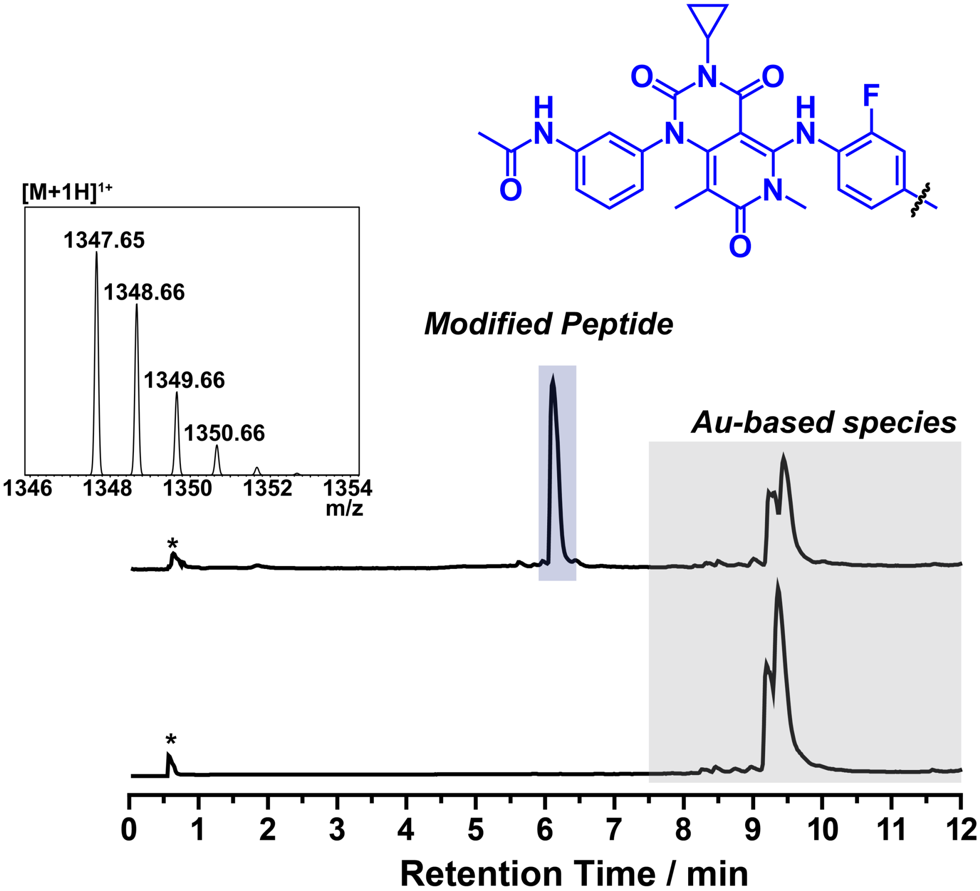
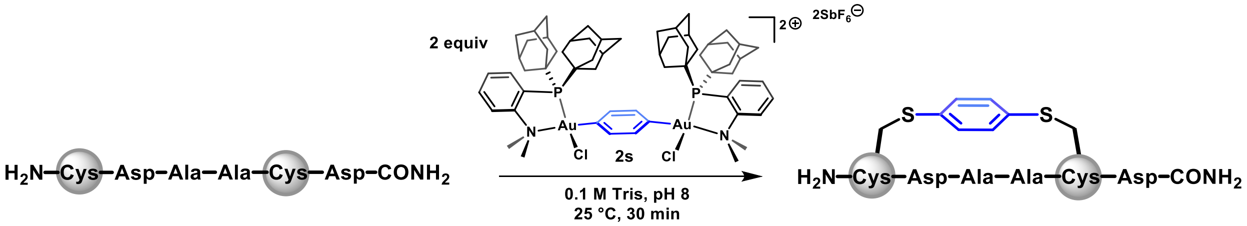


Figure S94. LC-MS trace of unprotected peptide modified with [**2n**][SbF$_6$] (top) as well as a control in which no peptide was added (bottom). (*) indicate Tris buffer (122 *m/z*). 1347.6594 (calc'd 1347.6539) *m/z* for $C_{60}H_{87}FN_{20}O_{13}S$.

Peptide Stapling Procedure



To a solution of the peptide (H_2N-CDAACD-$CONH_2$) in H_2O (2.8 mM, 5 mL, 0.2 M Tris, pH 8) was added a solution of [**2s**][SbF_6]$_2$ in MeCN (5.6 mM, 5 mL). The suspension was sonicated for 1 min, and then allowed to stand at 25 °C for a total of 30 min, at which point the reaction mixture was diluted with a 50/50 mixture of MeCN/H_2O containing 0.1%TFA, and the resulting suspension was centrifuged for 2 min. The supernatant was decanted and passed through a 0.45 µm filter. The filtrate was lyophilized and the obtained solid was dissolved in H_2O containing 0.1% TFA and purified by semi-preparative reversed-phase HPLC.

Solvent compositions for reversed-phase HPLC purification were: H_2O with 0.1% TFA (solvent A), MeCN with 0.1% TFA (solvent B). 0-5 min, 100% A; 5-60 min, linear gradient 100-60% A; 65-75 min, linear gradient 40-100% B. Flow rate: 3 mL/min. HPLC fractions containing the pure product were further confirmed by LC-MS, combined, and lyophilized.

Double Arylation of Dicysteine Peptide

To an Eppendorf tube containing 20 µL H_2O was added 50 µL (1.0 equiv) of a 2 mM solution of the peptide (H_2N-CDAACD-$CONH_2$) in H_2O (0.2 M Tris, pH 8). To this tube was added 40 µL (6.0 equiv) of a 15 mM solution of [**2m**][SbF_6] in MeCN. The reaction mixture was vortexed for 5 sec, and then allowed to stand for 5 min. A 20 µL aliquot of this solution was diluted with 100 µL of a 50/50 mixture of MeCN/H_2O containing 0.1%TFA, and the resulting solution was analyzed by LC-MS.

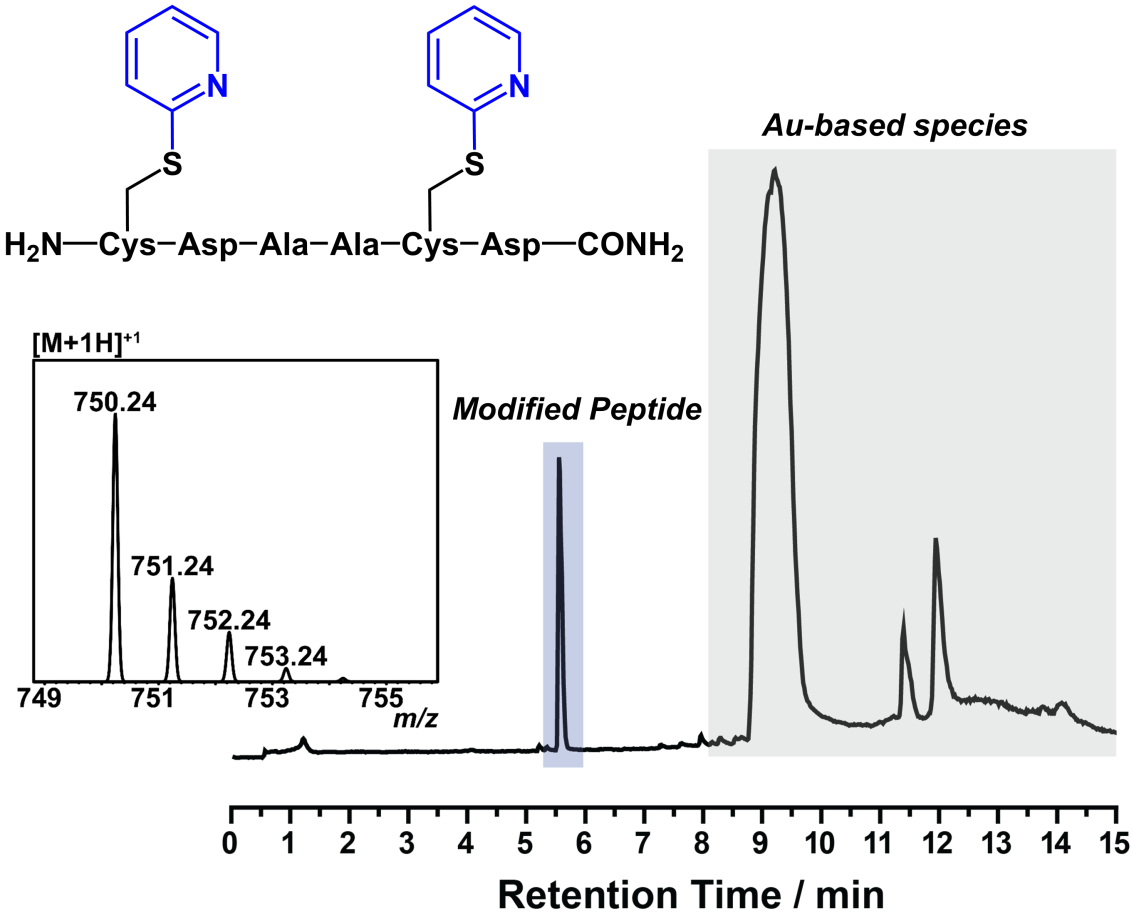


Figure S95. LC-MS trace of di-arylated peptide. 750.2395 (calc'd 750.2334) *m/z* for $C_{30}H_{39}N_9O_{10}S_2$.

Trypsin Digest and MS/MS experiments:

Trypsin digest experiment was performed by combining 50 µL of a 2 mM solution of peptide, 30 µL of water, and 20 µL of a 15 mM solution of [**2a**][SbF_6] or [**2i**][SbF_6], vortexing for <5 seconds and sitting at room temperature for 1 minute. After 1 minute, 20 µL of a 1 mg/mL solution of trypsin in water was added, vortexed for <5 seconds, and heated to 37 °C for 10 minutes. A 20 µL aliquot was taken from the mixture and added to 100 µL of a 50:50 (H_2O:MeCN 0.1% TFA) solution and analyzed via LC-MS.

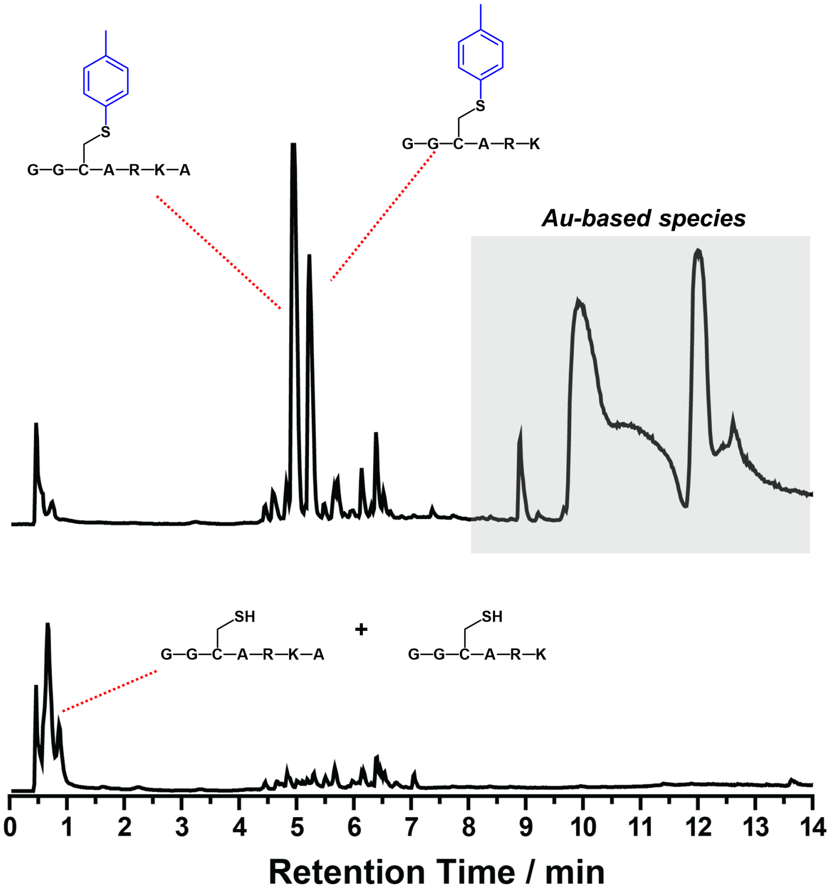


Figure S96. LC-MS traces of trypsin digest experiment of modified peptide (top) and native peptide (bottom).

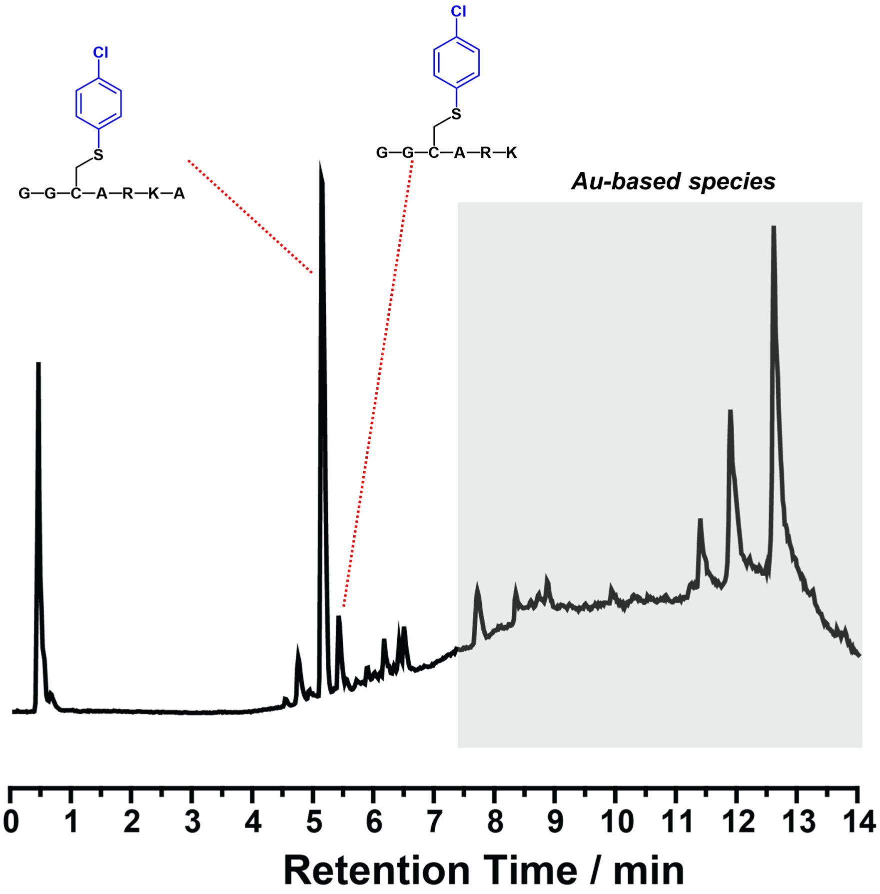


Figure S97. LC-MS trace of trypsin digested peptide modified with [**2i**][SbF_6].

Name	Ion Type	Ion Number	Theoretical Mass	Observed Mass
B3	B	3	290.0812	290.0839
B4	B	4	361.1184	361.1214
B5	B	5	464.1275	464.1304
Y1	Y	1	133.0615	133.0603
Y2	Y	2	236.0707	236.0729
Y3	Y	3	307.1078	307.1100
Y4	Y	4	378.1449	378.1470

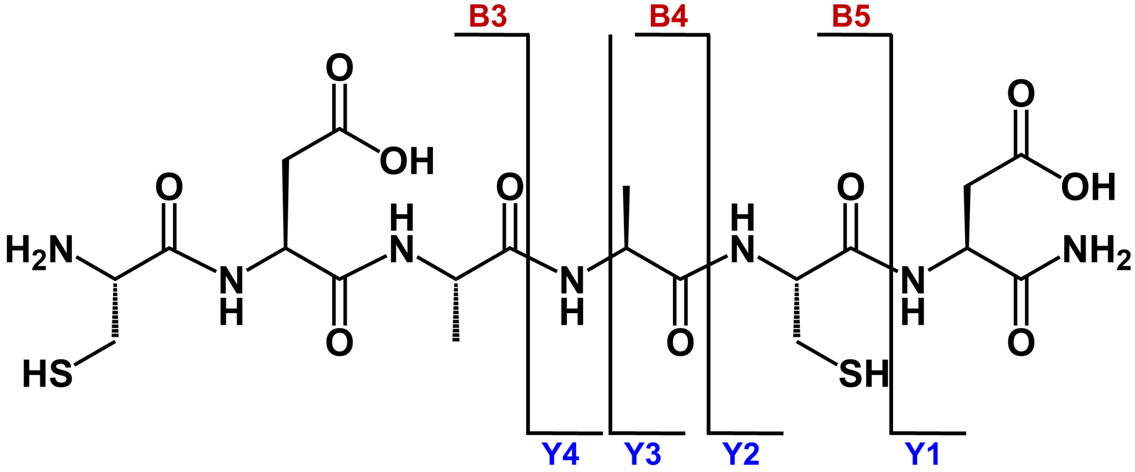


Figure S98. MS/MS analysis of dicysteine peptide, H_2N-CDAACD-$CONH_2$.

Name	Ion Type	Ion Number	Theoretical Mass	Observed Mass
B5	B	2	538.14	538.14

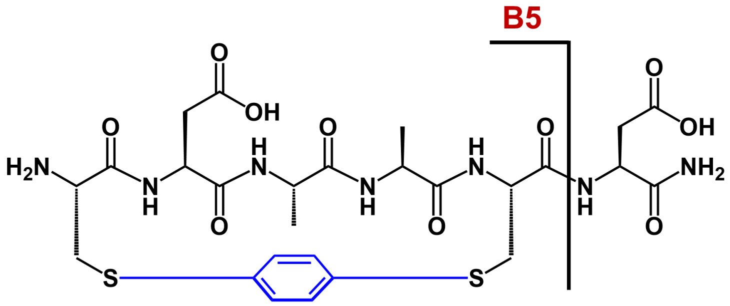


Figure S99. MS/MS analysis of stapled peptide.

Name	Ion Type	Ion Number	Theoretical Mass	Observed Mass
B4	B	4	314.1830	314.1292
B5	B	5	417.1922	417.1956
B7	B	7	644.3304	644.3294
Y2	Y	2	217.1666	217.1648
Y7	Y	7	661.3569	661.3562

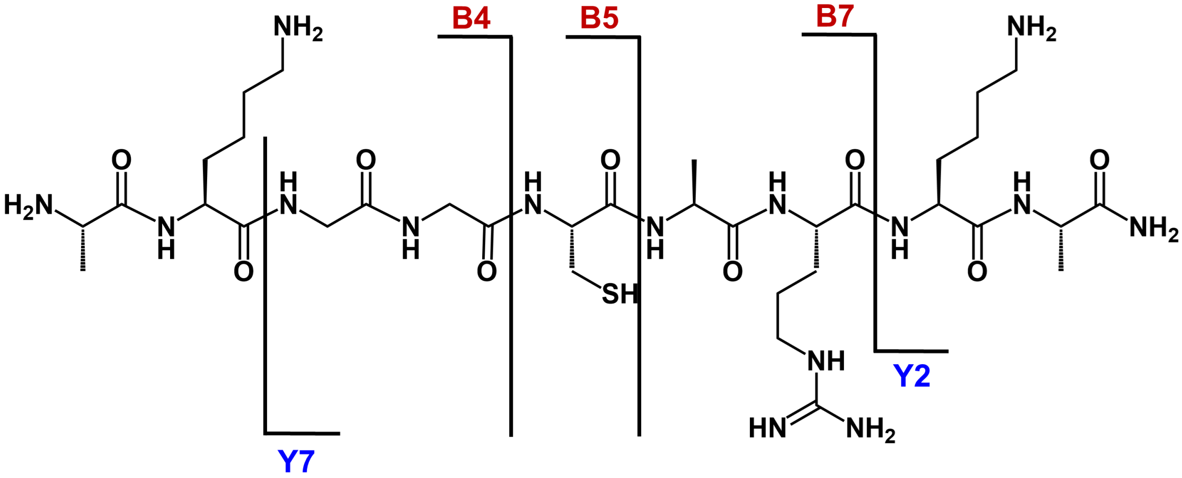


Figure S100. MS/MS analysis of native peptide sequence used for conjugation.

Name	Ion Type	Ion Number	Theoretical Mass	Observed Mass
B2	B	2	200.1401	200.1396
B5	B	5	527.1822	527.1848
B6	B	6	598.2193	598.2230
B7	B	7	754.3204	754.3204
B8	B	8	882.4154	882.4147
Y2	Y	2	217.1666	217.1663
Y3	Y	3	373.2677	373.2673
Y4	Y	4	444.3048	444.3040
Y6	Y	6	714.3255	714.3057
Y7	Y	7	771.3469	771.3470

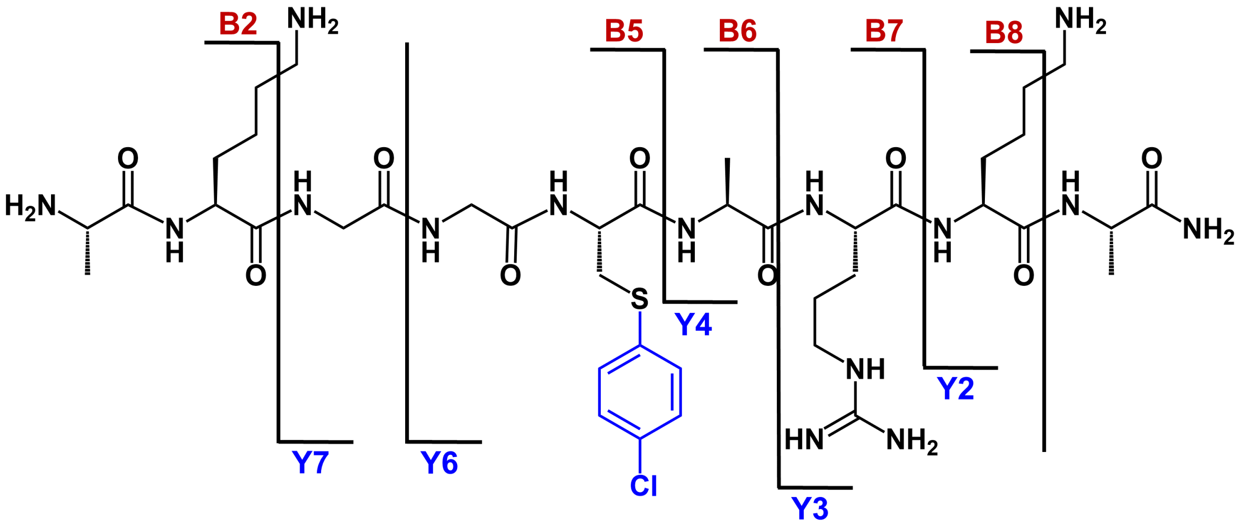


Figure S101. MS/MS analysis of arylated peptide.

Procedure for protein modifications

DARPin Modification: 50 µL of a 72.9 µM solution of DARPin in 20 mM Tris, 150 mM NaCl (pH: 7.5) was added to an Eppendorf tube. To this was added 45 µL of water and 5 µL of a 7.3 mM solution of **2a** in DMF. The solution was pipetted 20 times to ensure proper mixing and allowed to stand at room temperature for 30 min. After 30 min, a 20 µL aliquot of the reaction mixture was added to 100 µL of a 50:50 water/acetonitrile 0.1% TFA solution.

FGF2 Modification: 50 µL of a 0.66 µM solution of FGF2 in 200 mM Tris (pH 8.7) was added to an Eppendorf tube. To this solution was added 50 µL of a 9.93 µM solution of **2g** in water. The reaction m mixture was pipetted 20 times to ensure proper mixing and allowed to stand at room temperature for 30 min. After 30 min, a 20 µL aliquot of the reaction mixture was added to 100 µL of a 50:50 water/acetonitrile 0.1% TFA solution.

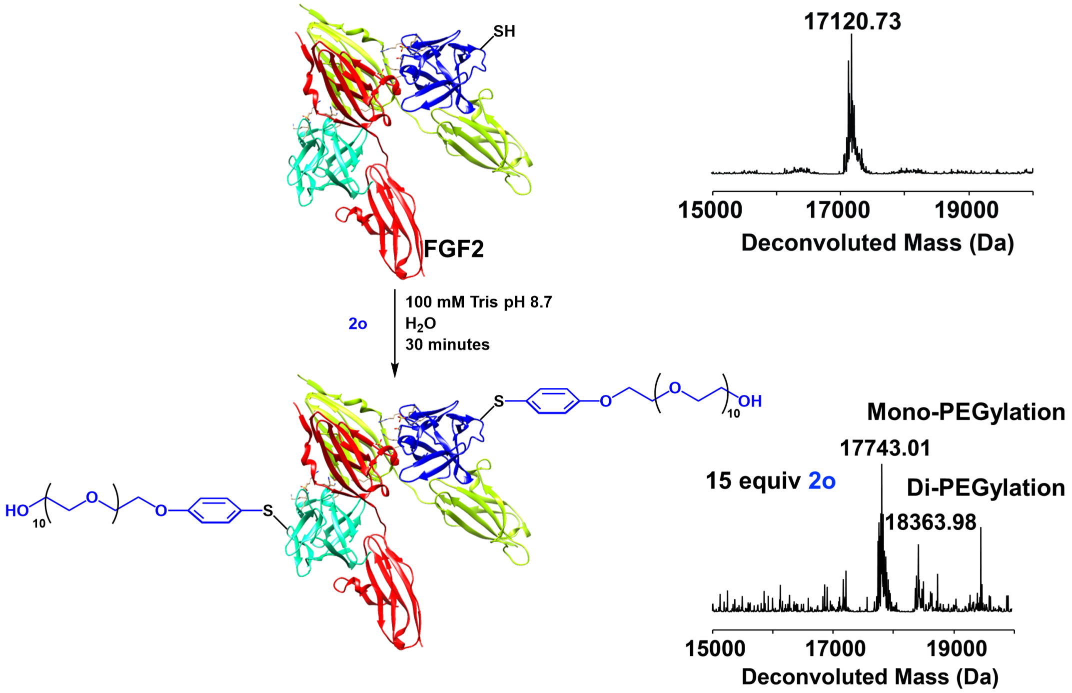
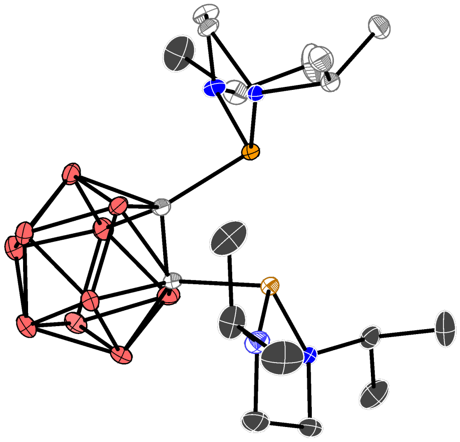


Figure S102. Modification of FGF2 using **2o** and corresponding masses. Di-PEGylation is consistent with the presence of two accessible cysteine residues.

V. X-Ray Crystallographic Data



Solid-state structure of DPCb with thermal ellipsoids rendered at the 50% probability level and with hydrogen atoms omitted for clarity.

Crystallographic Data for 1,2-bis(1,3-diisopropyl-1,3-2-diaminophosphino)-1,2-dicarba-*closo*-dodecaborane (DPCb).

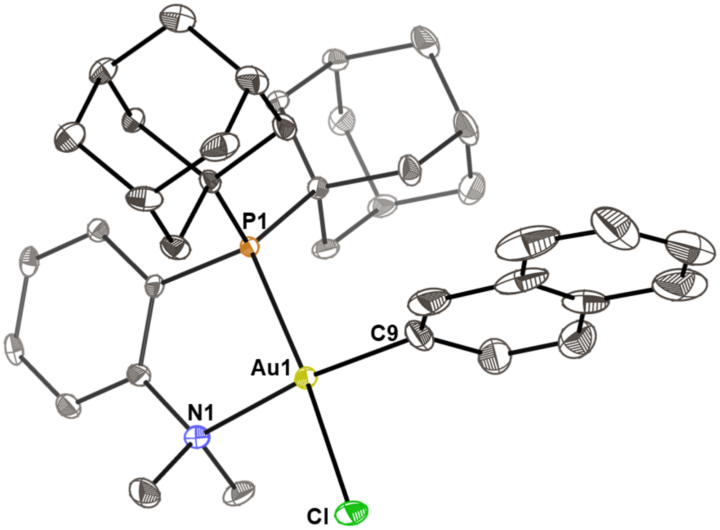
Identification code	MSM-A-2-221	
CCDC Code	1836204	
Empirical formula	C18 H46 B10 N4 P2	
Formula weight	488.63	
Temperature	100.15 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 11.492(2) Å	α = 90°
	b = 19.277(3) Å	β = 99.819(5)°
	c = 13.003(2) Å	γ = 90°
Volume	2838.3(8) $Å^3$	
Z	4	
Density (calculated)	1.143 Mg/m^3	
Absorption coefficient	0.169 mm^{-1}	
F(000)	1048	
Crystal size	0.27 x 0.23 x 0.12 mm^3	
Theta range for data collection	2.086 to 27.120°.	
Index ranges	$-14 \leq h \leq 14$, $-24 \leq k \leq 22$, $-16 \leq l \leq 16$	
Reflections collected	20897	
Independent reflections	6265 [R(int) = 0.0409]	
Completeness to theta = 25.242°	99.9%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.2612 and 0.2263	
Refinement method	Full-matrix least-squares on F^2	

Data / restraints / parameters	6265 / 0 / 315
Goodness-of-fit on F^2	1.023
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0418$, w$R_2 = 0.0958$
R indices (all data)	$R1 = 0.0619$, w$R2 = 0.1062$
Extinction coefficient	n/a
Largest diff. peak and hole	0.326 and -0.259 e.Å^{-3}

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for 1,2-bis(1,3-diisopropyl-1,3-2-diaminophosphino)-1,2-dicarba-*closo*-dodecaborane (DPCb). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
P(1)	2021(1)	3922(1)	3137(1)	13(1)
P(2)	4592(1)	3186(1)	3011(1)	12(1)
N(1)	591(1)	4152(1)	2885(1)	19(1)
N(2)	2102(1)	4047(1)	4434(1)	16(1)
N(3)	4414(1)	3522(1)	1802(1)	14(1)
N(4)	5655(1)	2614(1)	2821(1)	16(1)
C(1)	3292(2)	2555(1)	2925(1)	13(1)
C(2)	2014(2)	2913(1)	3113(1)	13(1)
C(3)	4933(2)	3052(1)	1107(1)	16(1)
C(4)	5964(2)	2668(1)	1771(1)	20(1)
C(5)	4585(2)	4280(1)	1701(1)	17(1)
C(6)	3880(2)	4538(1)	677(2)	23(1)
C(7)	5884(2)	4485(1)	1817(2)	22(1)
C(8)	6593(2)	2450(1)	3714(1)	20(1)
C(9)	7507(2)	3026(1)	3935(2)	33(1)
C(10)	7169(2)	1761(1)	3555(2)	35(1)
C(11)	34(2)	4070(1)	3812(2)	27(1)
C(12)	976(2)	4251(1)	4728(2)	24(1)
C(13)	-165(2)	4261(1)	1868(2)	29(1)
C(14)	-851(2)	4931(1)	1856(2)	45(1)
C(15)	531(2)	4250(1)	986(2)	36(1)
C(16)	3200(2)	4336(1)	5035(1)	19(1)
C(17)	3295(2)	5119(1)	4910(2)	32(1)
C(18)	3322(2)	4124(1)	6172(2)	30(1)
B(9)	2865(2)	2481(1)	4131(2)	17(1)
B(4)	850(2)	2436(1)	2491(2)	16(1)
B(2)	3048(2)	1818(1)	2176(2)	16(1)
B(8)	3505(2)	1772(1)	3550(2)	18(1)
B(1)	2134(2)	2564(1)	1910(2)	15(1)
B(7)	2333(2)	1232(1)	2924(2)	21(1)

B(10)	2234(2)	1645(1)	4140(2)	21(1)
B(5)	1310(2)	2381(1)	3862(2)	18(1)
B(3)	1486(2)	1729(1)	1898(2)	19(1)
B(6)	981(2)	1614(1)	3122(2)	21(1)



Solid-state structure of [**2c**][SbF$_6$] with thermal ellipsoids rendered at the 50% probability level and with hydrogen atoms, and [SbF$_6$]$^-$ counterion omitted for clarity.

Crystallographic Data for [**2c**][SbF$_6$].

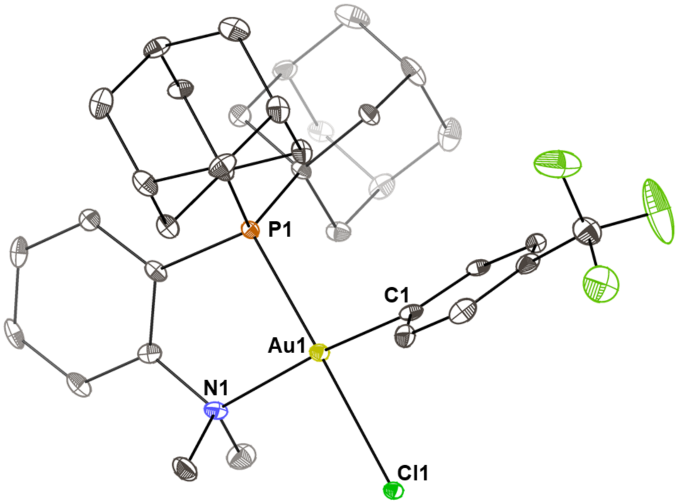
Identification code	JS-06	
CCDC Code	1835370	
Empirical formula	C38 H47 Au Cl F6 N P Sb	
Formula weight	1016.90	
Temperature	100.0 K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	*P*-1	
Unit cell dimensions	*a* = 10.0473(12) Å	α = 100.731(4)°
	b = 11.3493(14) Å	β = 103.700(4)°
	c = 17.4404(18) Å	γ = 99.465(4)°
Volume	1852.5(4) Å^3	
Z	2	
Density (calculated)	1.823 Mg/m^3	
Absorption coefficient	4.859 mm^{-1}	
F(000)	996	
Crystal size	0.3 x 0.22 x 0.08 mm^3	
Theta range for data collection	1.871 to 28.288°.	
Index ranges	$-13 \leq h \leq 13$, $-15 \leq k \leq 15$, $-21 \leq l \leq 23$	
Reflections collected	24139	
Independent reflections	9144 [*R*(int) = 0.0292]	
Completeness to theta = 25.242°	99.9%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.5633 and 0.3777	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9144 / 0 / 444	
Goodness-of-fit on F^2	1.033	

Final R indices $[I > 2\sigma(I)]$	$R1 = 0.0359$, $wR2 = 0.0734$
R indices (all data)	$R1 = 0.0443$, $wR2 = 0.0762$
Largest diff. peak and hole	2.306 and -2.007 e.Å^{-3}
SQUEEZE	Found 47e/uc; calc'd for CH_2Cl_2, 42e/uc

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for [**2c**][SbF_6]. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Au(1)	1025(1)	7043(1)	2269(1)	18(1)
Sb(1)	1335(1)	12273(1)	4024(1)	15(1)
Cl(1)	-1344(1)	7042(1)	1699(1)	28(1)
P(1)	3291(1)	6854(1)	2832(1)	13(1)
F(5)	2351(3)	13520(2)	3687(2)	29(1)
F(2)	327(3)	11051(2)	4384(2)	30(1)
N(1)	610(4)	6710(3)	3391(2)	18(1)
F(3)	1681(3)	13345(3)	5051(2)	31(1)
C(9)	1293(5)	7600(6)	1270(4)	34(1)
C(14)	1318(6)	8915(6)	1334(4)	38(1)
F(6)	999(3)	11198(3)	3014(2)	37(1)
C(13)	1360(6)	9415(5)	684(4)	40(1)
C(4)	1683(5)	6323(4)	4721(3)	19(1)
C(31)	3519(5)	2765(4)	1920(3)	23(1)
F(1)	-310(3)	12824(3)	3654(2)	39(1)
C(32)	4924(5)	3708(4)	2234(3)	19(1)
C(1)	-588(5)	5635(5)	3218(4)	31(1)
F(4)	2991(3)	11761(3)	4414(2)	31(1)
C(30)	5423(5)	3996(5)	1514(3)	25(1)
C(8)	3112(4)	6545(4)	3795(3)	14(1)
C(27)	2433(5)	3303(4)	1400(3)	23(1)
C(12)	1392(5)	8638(5)	-12(4)	33(1)
C(34)	4180(5)	5729(4)	1517(3)	21(1)
C(3)	1829(4)	6521(4)	3979(3)	16(1)
C(2)	197(5)	7859(5)	3750(3)	28(1)
C(33)	4730(4)	4879(4)	2764(3)	15(1)
C(20)	6165(4)	8111(4)	3446(3)	15(1)
C(19)	7225(4)	9364(4)	3678(3)	16(1)
C(25)	3651(4)	5447(4)	2237(3)	14(1)
C(26)	2240(4)	4476(4)	1923(3)	20(1)
C(10)	1290(5)	6883(6)	594(4)	41(2)

C(23)	5744(5)	10046(5)	2553(3)	30(1)
C(5)	2808(5)	6159(4)	5287(3)	18(1)
C(6)	4096(5)	6202(4)	5124(3)	17(1)
C(24)	4668(5)	8808(4)	2315(3)	24(1)
C(29)	4334(5)	4533(5)	999(3)	25(1)
C(16)	4282(4)	9234(4)	3707(3)	21(1)
C(7)	4242(4)	6385(4)	4389(3)	14(1)
C(21)	5355(5)	10958(4)	3182(4)	30(1)
C(28)	2922(5)	3600(5)	682(3)	29(1)
C(18)	6826(5)	10271(4)	4299(3)	21(1)
C(15)	4674(4)	8299(4)	3081(3)	17(1)
C(22)	7215(5)	9851(4)	2916(3)	25(1)
C(11)	1356(5)	7417(5)	-146(4)	43(2)
C(17)	5364(5)	10473(4)	3939(3)	24(1)
C(36)	1439(6)	8480(8)	-1435(4)	54(2)
C(37)	1434(6)	7235(9)	-1454(4)	60(2)
C(38)	1402(6)	6649(7)	-811(5)	61(2)
C(35)	1415(6)	9219(9)	-744(4)	60(2)



Solid-state structure of [**2d**][SbF_6] with thermal ellipsoids rendered at the 50% probability level and with hydrogen atoms, disorder and [SbF_6]$^-$ counterion omitted for clarity.

Crystal Data for [**2d**][SbF_6].

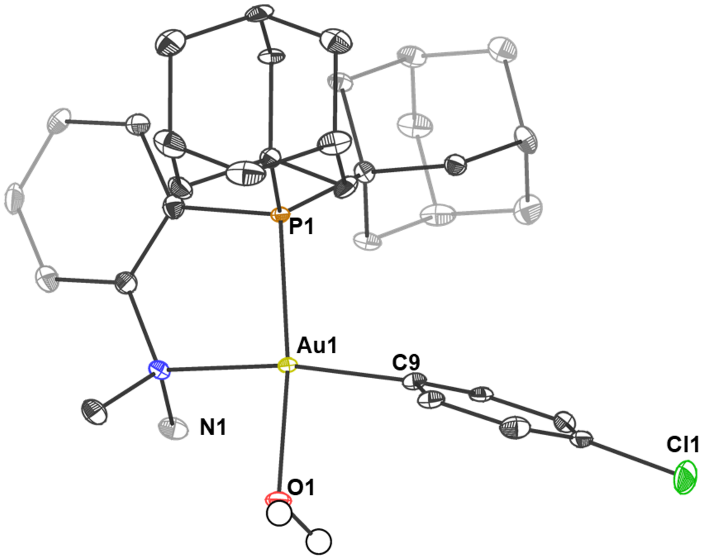
Identification code	JS-07	
CCDC Code	1835367	
Empirical formula	C35 H44 Au Cl0.86 F9 I0.14 N P Sb	
Formula weight	1047.65	
Temperature	100.0 K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	*P*-1	
Unit cell dimensions	*a* = 10.2214(4) Å	α = 108.9020(10)°
	b = 11.5151(4) Å	β = 99.9440(10)°
	c = 16.2248(6) Å	γ = 100.4260(10)°
Volume	1721.07(11) Å^3	
Z	2	
Density (calculated)	2.022 Mg/m^3	
Absorption coefficient	5.358 mm^{-1}	
F(000)	1018	
Crystal size	0.3 x 0.27 x 0.21 mm^3	
Theta range for data collection	1.916 to 28.267°.	
Index ranges	$-12 \leq h \leq 13$, $-15 \leq k \leq 15$, $-21 \leq l \leq 21$	
Reflections collected	23765	
Independent reflections	8525 [*R*(int) = 0.0402]	
Completeness to theta = 25.242°	99.9%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.5633 and 0.4649	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8525 / 0 / 436	
Goodness-of-fit on F^2	1.035	

Final *R* indices [$I > 2\sigma(I)$]	$R1 = 0.0326$, $wR2 = 0.0604$
R indices (all data)	$R1 = 0.0459$, $wR2 = 0.0644$
Extinction coefficient	n/a
Largest diff. peak and hole	2.688 and -1.864 e.Å^{-3}

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for [**2d**][SbF$_6$]. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Au(1)	6102(1)	6560(1)	7210(1)	11(1)
Sb(1)	6396(1)	11976(1)	8925(1)	15(1)
Cl(1)	3712(2)	6382(2)	6713(1)	11(1)
P(1)	8366(1)	6482(1)	7673(1)	10(1)
F(6)	7311(3)	13222(3)	8563(2)	28(1)
F(5)	7111(3)	13094(3)	10129(2)	27(1)
F(4)	5495(3)	10762(3)	9309(2)	34(1)
F(8)	4860(3)	12657(3)	8878(2)	26(1)
F(3)	6033(3)	9529(3)	4118(2)	33(1)
F(9)	7936(3)	11320(3)	9000(2)	36(1)
F(7)	5712(3)	10895(3)	7725(2)	41(1)
F(1)	8059(3)	9275(3)	4309(2)	43(1)
N(1)	5807(4)	6279(3)	8437(2)	13(1)
F(2)	6408(5)	7801(3)	3307(2)	60(1)
C(1)	6259(4)	7107(4)	6154(3)	13(1)
C(15)	9728(4)	7935(4)	7853(3)	11(1)
C(12)	9416(5)	6292(4)	10188(3)	15(1)
C(4)	6490(4)	8096(4)	4822(3)	16(1)
C(27)	9059(5)	5024(4)	6115(3)	14(1)
C(26)	8623(4)	4934(4)	6963(3)	10(1)
C(6)	6355(4)	6330(4)	5321(3)	13(1)
C(34)	9730(4)	4501(4)	7489(3)	14(1)
C(13)	9489(4)	6389(4)	9365(3)	13(1)
C(11)	8181(5)	6157(4)	10417(3)	18(1)
C(5)	6471(4)	6825(4)	4659(3)	14(1)
C(16)	9471(5)	9046(4)	8606(3)	14(1)
C(22)	11203(4)	7807(4)	8136(3)	15(1)
C(24)	10528(5)	10281(4)	8777(3)	16(1)
C(9)	7075(4)	6265(4)	9019(3)	12(1)
C(18)	10387(5)	10581(4)	7918(3)	17(1)
C(2)	6210(4)	8358(4)	6299(3)	17(1)

C(30)	9863(4)	3201(4)	6877(3)	16(1)
C(3)	6333(4)	8852(4)	5642(3)	16(1)
C(19)	10658(5)	9500(4)	7174(3)	16(1)
C(10)	7012(5)	6148(4)	9841(3)	17(1)
C(28)	9159(5)	3722(4)	5520(3)	20(1)
C(21)	12245(5)	9068(4)	8319(3)	17(1)
C(35)	7775(5)	2744(4)	5253(3)	21(1)
C(14)	8305(4)	6373(4)	8769(3)	11(1)
C(25)	9607(4)	8257(4)	6988(3)	14(1)
C(31)	8505(4)	2215(4)	6609(3)	15(1)
C(29)	10284(5)	3328(4)	6044(3)	22(1)
C(017)	6733(5)	8661(4)	4129(3)	22(1)
C(7)	4705(5)	5111(4)	8243(3)	23(1)
C(20)	12113(5)	9372(4)	7461(3)	18(1)
C(32)	7384(5)	2620(4)	6089(3)	17(1)
C(33)	7249(4)	3924(4)	6682(3)	14(1)
C(23)	11979(5)	10133(4)	9064(3)	18(1)
C(8)	5364(5)	7447(4)	8925(3)	21(1)
I(1)	3551(3)	6512(3)	6725(2)	11(1)



Solid-state structure of [(Me-DalPhos)Au(*p*-Cl-C_6H_4)OH_2][SbF_6]$_2$ with thermal ellipsoids rendered at the 50% probability level and with selected hydrogen atoms, disorder, two [SbF_6]$^-$ counterions and one DCM molecule omitted for clarity.

Crystallographic Data for [(Me-DalPhos)Au(*p*-Cl-C_6H_4)OH_2][SbF_6]$_2$.

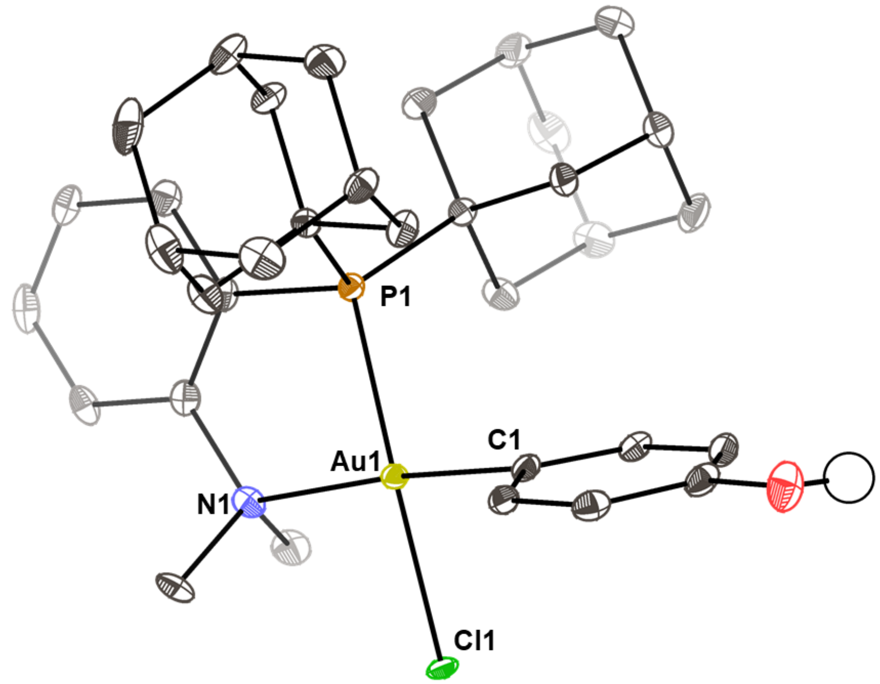
Identification code	JS-08	
CCDC Code	1835368	
Empirical formula	C70 H95 Au2 Cl6 F18 N2 O2 P2 Sb3	
Formula weight	2372.30	
Temperature	100.0 K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	*P*-1	
Unit cell dimensions	a = 10.3978(4) Å	α = 90.4650(10)°
	b = 10.8778(4) Å	β = 90.5830(10)°
	c = 17.7061(7) Å	γ = 94.1330(10)°
Volume	1997.26(13) $Å^3$	
Z	1	
Density (calculated)	1.972 Mg/m^3	
Absorption coefficient	4.989 mm^{-1}	
F(000)	1150	
Crystal size	0.25 x 0.2 x 0.15 mm^3	
Theta range for data collection	1.877 to 28.297°.	
Index ranges	$-13 \le h \le 13$, $-14 \le k \le 14$, $-20 \le l \le 23$	
Reflections collected	35922	
Independent reflections	9931 [*R*(int) = 0.0460]	
Completeness to theta = 25.242°	100.0%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7457 and 0.6326	
Refinement method	Full-matrix least-squares on F^2	

Data / restraints / parameters	9931 / 3 / 483
Goodness-of-fit on F^2	1.010
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0294$, $wR2 = 0.0529$
R indices (all data)	$R1 = 0.0411$, $wR2 = 0.0560$
Extinction coefficient	n/a
Largest diff. peak and hole	1.184 and -1.134 e.Å^{-3}

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for [(Me-DalPhos)Au(*p*-Cl-C_6H_4)OH_2][SbF_6]$_2$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Au(1)	4358(1)	3696(1)	3656(1)	9(1)
Sb(1)	8445(1)	2689(1)	4772(1)	19(1)
Sb(2)	0	0	0	25(1)
P(1)	3440(1)	3112(1)	2514(1)	9(1)
Cl(1)	7351(1)	9156(1)	3384(1)	26(1)
Cl(2)	5598(1)	7420(1)	1479(1)	32(1)
Cl(3)	7534(1)	6345(1)	558(1)	41(1)
F(6)	9644(2)	2832(2)	5568(1)	32(1)
F(2)	7790(2)	4204(2)	5056(2)	31(1)
O(1)	5134(2)	4002(2)	4720(1)	14(1)
F(4)	7193(2)	2579(2)	3987(1)	34(1)
F(1)	9016(2)	1159(2)	4506(2)	37(1)
F(3)	7214(2)	1901(2)	5407(1)	31(1)
F(5)	9606(2)	3510(3)	4123(2)	44(1)
N(1)	3293(3)	2092(3)	4115(2)	12(1)
C(35)	5792(3)	3617(3)	1786(2)	15(1)
C(22)	3046(3)	5347(3)	1805(2)	13(1)
F(8)	-578(3)	-488(3)	941(2)	74(1)
C(9)	5296(3)	5362(3)	3403(2)	13(1)
C(2)	4230(3)	1262(3)	4454(2)	17(1)
C(16)	1291(3)	3663(3)	1583(2)	13(1)
F(9)	-1691(3)	-237(4)	-334(2)	87(1)
C(23)	1558(3)	4624(3)	2867(2)	14(1)
C(33)	4129(3)	2294(3)	1061(2)	14(1)
C(7)	1699(3)	1020(3)	2281(2)	16(1)
C(26)	4687(3)	2611(3)	1852(2)	12(1)
C(30)	6846(3)	3171(3)	1270(2)	18(1)
C(31)	6281(4)	2858(3)	481(2)	19(1)
C(11)	7253(3)	6669(3)	3299(2)	17(1)
C(15)	2297(3)	4229(3)	2161(2)	11(1)

C(14)	4612(3)	6407(3)	3495(2)	11(1)
C(13)	5229(3)	7577(3)	3476(2)	15(1)
C(1)	2484(3)	2601(3)	4722(2)	17(1)
C(21)	2095(3)	6323(3)	1596(2)	17(1)
C(5)	912(4)	-289(3)	3284(2)	21(1)
C(17)	366(3)	4650(3)	1362(2)	16(1)
C(6)	921(4)	20(3)	2524(2)	20(1)
C(10)	6623(3)	5498(3)	3320(2)	13(1)
C(32)	5194(4)	1842(3)	555(2)	17(1)
C(29)	7385(4)	2023(4)	1617(2)	23(1)
C(20)	1388(4)	6715(3)	2305(2)	24(1)
C(24)	627(3)	5597(3)	2643(2)	19(1)
C(18)	-346(3)	5047(4)	2064(2)	21(1)
C(25)	1119(3)	5770(3)	1013(2)	18(1)
C(4)	1677(3)	388(3)	3796(2)	18(1)
C(3)	2460(3)	1390(3)	3556(2)	13(1)
C(8)	2463(3)	1742(3)	2802(2)	14(1)
C(27)	5235(4)	1445(3)	2199(2)	18(1)
F(7)	-224(4)	1600(3)	284(3)	113(2)
C(12)	6558(3)	7697(3)	3379(2)	15(1)
C(36)	7161(4)	7618(4)	1118(3)	34(1)
C(34)	5725(4)	697(3)	899(2)	24(1)
C(28)	6306(4)	1013(4)	1678(2)	23(1)



Solid-state structure of [**2f**][SbF_6]·H_2O with thermal ellipsoids rendered at the 50% probability level and with selected hydrogen atoms, one water molecule, and [SbF_6]$^-$ counterion omitted for clarity.

Crystallographic Data for [**2f**][SbF_6]·H_2O.

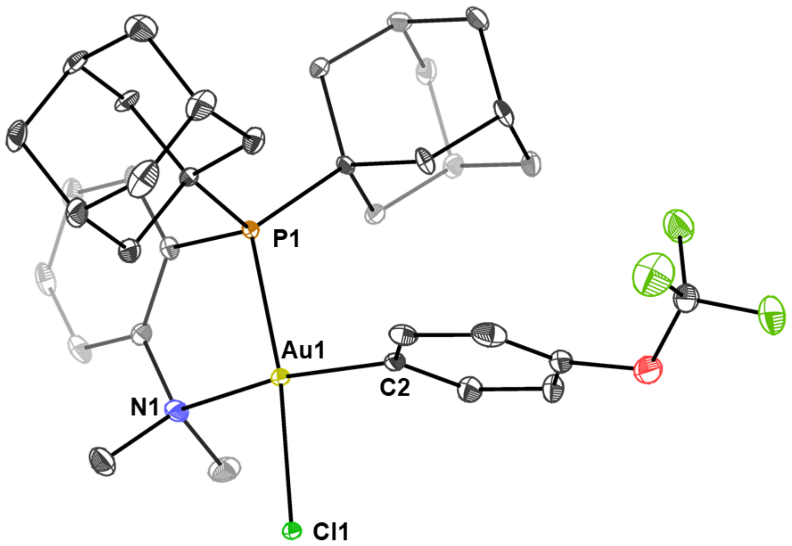
Identification code	JS-13	
CCDC Code	1835373	
Empirical formula	C34 H47 Au Cl F6 N O2 P Sb	
Formula weight	1000.86	
Temperature	100.0 K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	*P*-1	
Unit cell dimensions	*a* = 9.5384(10) Å	α = 112.015(2)°
	b = 13.2116(13) Å	β = 105.708(2)°
	c = 15.7777(11) Å	γ = 91.052(3)°
Volume	1758.4(3) Å^3	
Z	2	
Density (calculated)	1.890 Mg/m^3	
Absorption coefficient	5.121 mm^{-1}	
F(000)	980	
Crystal size	0.3 x 0.28 x 0.18 mm^3	
Theta range for data collection	1.459 to 28.284°.	
Index ranges	$-11 \leq h \leq 12$, $-17 \leq k \leq 17$, $-18 \leq l \leq 21$	
Reflections collected	31512	
Independent reflections	8736 [*R*(int) = 0.0381]	
Completeness to theta = 25.242°	99.9%	

Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.5633 and 0.4270
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8736 / 0 / 438
Goodness-of-fit on F^2	1.024
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0256$, $wR2 = 0.0516$
R indices (all data)	$R1 = 0.0337$, $wR2 = 0.0543$
Extinction coefficient	n/a
Largest diff. peak and hole	1.022 and -0.862 e.Å^{-3}

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) For [**2f**][SbF_6]·H_2O. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Au(1)	8596(1)	4062(1)	2777(1)	11(1)
Sb(1)	10000	5000	0	15(1)
Sb(2)	10000	0	5000	22(1)
Cl(1)	11133(1)	4665(1)	3506(1)	15(1)
P(1)	6074(1)	3560(1)	2242(1)	12(1)
F(1)	10141(4)	4357(3)	867(2)	81(1)
F(2)	12018(3)	5138(2)	260(2)	64(1)
F(3)	10179(3)	6378(2)	998(2)	51(1)
F(4)	11012(3)	-884(2)	4190(2)	49(1)
F(5)	8253(3)	-605(2)	3998(2)	50(1)
F(6)	10222(3)	1120(2)	4585(2)	48(1)
O(1)	10888(3)	-417(2)	1248(2)	26(1)
O(2)	11532(3)	-1563(2)	2394(2)	33(1)
N(1)	8118(3)	5775(2)	3277(2)	15(1)
C(1)	9215(3)	2529(2)	2280(2)	14(1)
C(2)	9654(3)	2231(3)	1454(2)	16(1)
C(3)	10211(4)	1244(3)	1121(2)	18(1)
C(4)	10337(4)	548(3)	1614(2)	19(1)
C(5)	9921(3)	859(3)	2445(2)	18(1)
C(6)	9388(3)	1861(3)	2786(2)	15(1)
C(7)	8916(4)	6355(3)	2854(3)	22(1)
C(8)	8713(4)	6281(3)	4348(2)	21(1)
C(9)	6531(4)	5863(3)	2991(2)	15(1)
C(10)	6091(4)	6911(3)	3186(2)	17(1)
C(11)	4612(4)	7020(3)	2965(2)	21(1)
C(12)	3567(4)	6105(3)	2582(2)	18(1)
C(13)	3998(4)	5071(3)	2388(2)	17(1)
C(14)	5485(3)	4931(3)	2580(2)	14(1)
C(15)	5526(3)	2895(2)	2984(2)	13(1)
C(16)	6569(4)	3505(3)	4020(2)	17(1)
C(17)	6215(4)	2992(3)	4681(2)	22(1)

C(18)	4619(4)	3108(3)	4687(3)	25(1)
C(19)	3590(4)	2492(3)	3674(3)	21(1)
C(20)	3800(4)	1271(3)	3319(3)	23(1)
C(21)	5388(4)	1171(3)	3306(2)	20(1)
C(22)	5683(4)	1658(3)	2616(2)	16(1)
C(23)	3926(4)	3011(3)	3014(3)	19(1)
C(24)	6435(4)	1784(3)	4320(3)	23(1)
C(25)	5286(3)	2848(2)	908(2)	13(1)
C(26)	3584(3)	2599(3)	558(2)	18(1)
C(27)	3048(4)	2058(3)	-547(2)	21(1)
C(28)	3543(4)	2850(3)	-945(3)	28(1)
C(29)	5211(4)	3085(3)	-619(2)	25(1)
C(30)	5865(4)	2009(3)	-965(2)	24(1)
C(31)	5363(4)	1229(3)	-564(2)	18(1)
C(32)	5903(4)	1749(3)	533(2)	17(1)
C(33)	5776(4)	3632(3)	488(2)	19(1)
C(34)	3684(4)	980(3)	-905(2)	21(1)



Solid-state structure of [**2g**][SbF_6] with thermal ellipsoids rendered at the 50% probability level and with hydrogen atoms, disorder, and [SbF_6]$^-$ counterion omitted for clarity.

Crystal data and structure refinement for [**2g**][SbF_6].

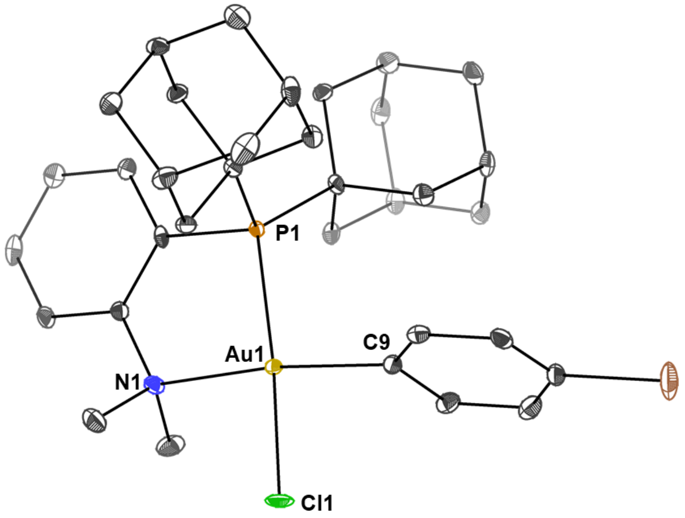
Identification code	JS-09	
CCDC Code	1835371	
Empirical formula	C35 H44 Au Cl0.95 F9 I0.05 N O P Sb	
Formula weight	1055.42	
Temperature	100.0 K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	*P*-1	
Unit cell dimensions	a = 10.0238(6) Å	α = 106.082(2)°
	b = 11.7115(7) Å	β = 106.450(2)°
	c = 16.7522(11) Å	γ = 97.925(2)°
Volume	1761.65(19) $Å^3$	
Z	2	
Density (calculated)	1.990 Mg/m^3	
Absorption coefficient	5.166 mm^{-1}	
F(000)	1028	
Crystal size	0.29 x 0.28 x 0.26 mm^3	
Theta range for data collection	1.344 to 28.316°.	
Index ranges	$-13 \leq h \leq 13$, $-14 \leq k \leq 15$, $-21 \leq l \leq 22$	
Reflections collected	30660	
Independent reflections	8761 [*R*(int) = 0.0353]	
Completeness to theta = 25.242°	100.0%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7457 and 0.5596	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8761 / 2 / 456	

Goodness-of-fit on F^2	1.026
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0267$, $wR2 = 0.0587$
R indices (all data)	$R1 = 0.0327$, $wR2 = 0.0611$
Extinction coefficient	n/a
Largest diff. peak and hole	2.624 and -0.785 e.Å^{-3}

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for [**2g**][SbF_6]. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Au(1)	6146(1)	5645(1)	7174(1)	10(1)
Sb(1)	2359(1)	-1787(1)	1095(1)	14(1)
Cl(1)	8027(2)	5307(2)	6550(1)	10(1)
P(1)	4358(1)	6222(1)	7717(1)	9(1)
F(2)	1233(3)	226(2)	4611(2)	29(1)
F(8)	1863(3)	-1783(2)	-77(2)	33(1)
F(9)	3668(3)	-274(2)	1457(2)	28(1)
F(4)	918(3)	-980(3)	1244(2)	35(1)
F(7)	3774(3)	-2607(3)	913(2)	38(1)
F(3)	1732(3)	-1167(2)	3677(2)	30(1)
F(1)	1301(3)	446(3)	3399(2)	38(1)
F(6)	1044(3)	-3292(2)	704(2)	32(1)
C(26)	3254(3)	5011(3)	7950(2)	10(1)
F(5)	2888(3)	-1761(3)	2259(2)	43(1)
O(1)	3331(3)	497(3)	4410(2)	27(1)
C(33)	4315(4)	4622(3)	8639(2)	12(1)
C(23)	2125(4)	6138(3)	6218(2)	15(1)
C(27)	2106(4)	5479(3)	8334(2)	13(1)
N(1)	7641(3)	7112(3)	8328(2)	14(1)
C(12)	7262(4)	9179(3)	10352(2)	18(1)
C(14)	4924(4)	7997(3)	9387(2)	12(1)
C(28)	1317(4)	4453(3)	8561(2)	14(1)
C(16)	3333(3)	7044(3)	7032(2)	9(1)
C(32)	3504(4)	3617(3)	8869(2)	13(1)
C(2)	5010(4)	4042(3)	6210(2)	13(1)
C(34)	2475(4)	3879(3)	7114(2)	13(1)
C(4)	3474(4)	2691(4)	4767(3)	22(1)
C(13)	5801(4)	8877(3)	10180(2)	16(1)
C(30)	1676(4)	2870(3)	7350(2)	15(1)
C(35)	2388(4)	4097(3)	9249(2)	15(1)
C(29)	558(4)	3339(3)	7731(2)	16(1)
C(22)	1398(4)	6830(4)	5623(3)	21(1)

C(18)	3656(4)	8444(4)	6149(3)	19(1)
C(11)	7845(4)	8598(3)	9739(2)	17(1)
C(10)	6967(4)	7709(3)	8949(2)	12(1)
C(3)	4088(4)	3890(4)	5379(2)	17(1)
C(011)	2484(5)	7516(4)	5338(3)	24(1)
C(8)	8648(4)	6447(4)	8760(3)	22(1)
C(17)	4421(4)	7754(3)	6732(3)	16(1)
C(1)	1935(4)	23(4)	4034(2)	18(1)
C(24)	2696(4)	7991(3)	7562(2)	14(1)
C(21)	738(4)	7744(4)	6150(3)	23(1)
C(5)	3819(4)	1718(4)	5020(3)	22(1)
C(31)	2752(4)	2501(3)	8030(2)	15(1)
C(25)	1916(4)	8664(3)	6965(3)	17(1)
C(19)	3003(4)	9363(3)	6678(3)	19(1)
C(15)	5484(4)	7387(3)	8759(2)	11(1)
C(6)	4733(4)	1855(4)	5831(3)	22(1)
C(9)	8456(4)	8050(4)	8075(3)	21(1)
C(7)	5344(4)	3021(4)	6431(3)	19(1)
I(1)	8258(7)	5184(9)	6574(5)	27(2)



Solid-state structure of [**2j**][SbF$_6$] with thermal ellipsoids rendered at the 50% probability level and with hydrogen atoms, disorder, and [SbF$_6$]$^-$ counterion omitted for clarity.

Crystallographic Data for [**2j**][SbF$_6$].

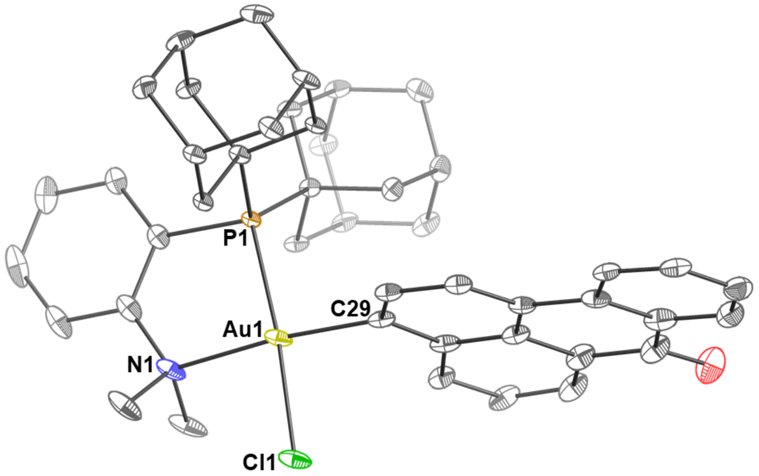
Identification code	JS-12	
CCDC Code	1835371	
Empirical formula	C34 H44 Au Br Cl0.77 F6 I0.23 N P Sb	
Formula weight	1066.78	
Temperature	100.0 K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	*P*-1	
Unit cell dimensions	a = 10.1820(10) Å	α = 109.033(4)°
	b = 11.4038(13) Å	β = 100.165(3)°
	c = 16.3043(16) Å	γ = 100.426(4)°
Volume	1702.7(3) Å^3	
Z	2	
Density (calculated)	2.081 Mg/m^3	
Absorption coefficient	6.646 mm^{-1}	
F(000)	1029	
Crystal size	0.26 x 0.24 x 0.18 mm^3	
Theta range for data collection	1.926 to 28.275°.	
Index ranges	$-13 \leq h \leq 13$, $-14 \leq k \leq 15$, $-21 \leq l \leq 21$	
Reflections collected	30650	
Independent reflections	8451 [*R*(int) = 0.0374]	
Completeness to theta = 25.242°	100.0%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7457 and 0.5487	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8451 / 2 / 418	
Goodness-of-fit on F^2	1.028	

Final R indices $[I > 2\sigma(I)]$	$R1 = 0.0276$, $wR2 = 0.0582$
R indices (all data)	$R1 = 0.0348$, $wR2 = 0.0604$
Extinction coefficient	n/a
Largest diff. peak and hole	1.913 and -3.742 e.Å^{-3}

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for [**2j**][SbF$_6$]. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Au(1)	1103(1)	1550(1)	7182(1)	9(1)
Sb(1)	1382(1)	6967(1)	8946(1)	12(1)
Br(1)	1456(1)	3684(1)	3837(1)	30(1)
P(1)	3370(1)	1458(1)	7651(1)	8(1)
F(1)	2285(3)	8172(2)	8535(2)	25(1)
F(2)	647(3)	5811(3)	7764(2)	32(1)
F(3)	2930(3)	6303(2)	9026(2)	30(1)
F(4)	497(3)	5794(2)	9376(2)	27(1)
F(5)	2132(2)	8154(2)	10132(2)	23(1)
F(6)	-160(2)	7656(2)	8884(2)	22(1)
N(1)	786(3)	1234(3)	8386(2)	12(1)
C(1)	-320(4)	25(4)	8158(3)	21(1)
C(2)	312(4)	2383(4)	8881(3)	20(1)
C(3)	2045(4)	1211(3)	8975(2)	11(1)
C(4)	3299(4)	1341(3)	8731(2)	10(1)
C(5)	4484(4)	1370(3)	9345(2)	12(1)
C(6)	4412(4)	1277(4)	10164(2)	15(1)
C(7)	3147(4)	1123(4)	10380(3)	16(1)
C(8)	1967(4)	1087(4)	9787(2)	14(1)
C(9)	1281(4)	2111(4)	6130(2)	12(1)
C(10)	1367(4)	1315(4)	5305(2)	12(1)
C(11)	1432(4)	1796(4)	4623(3)	15(1)
C(12)	1380(4)	3051(4)	4778(3)	18(1)
C(13)	1240(4)	3833(4)	5582(3)	18(1)
C(14)	1185(4)	3362(4)	6263(3)	15(1)
C(15)	3649(4)	-107(3)	6946(2)	10(1)
C(16)	4731(4)	-547(3)	7489(2)	13(1)
C(17)	4888(4)	-1848(3)	6887(3)	13(1)
C(18)	3504(4)	-2849(4)	6593(3)	16(1)
C(19)	2412(4)	-2440(4)	6051(3)	16(1)
C(20)	2855(5)	-2319(4)	5226(3)	21(1)
C(21)	4242(4)	-1321(4)	5528(3)	18(1)

C(22)	2254(4)	-1133(3)	6640(3)	12(1)
C(23)	5337(4)	-1728(4)	6066(3)	19(1)
C(24)	4119(4)	-3(4)	6118(2)	14(1)
C(25)	4739(4)	2926(3)	7845(2)	10(1)
C(26)	4626(4)	3268(4)	6991(2)	13(1)
C(27)	5689(4)	4543(4)	7199(3)	15(1)
C(28)	5411(4)	5616(4)	7947(3)	15(1)
C(29)	5546(4)	5290(3)	8791(2)	13(1)
C(30)	6999(4)	5149(4)	9088(3)	16(1)
C(31)	7274(4)	4078(4)	8334(3)	16(1)
C(32)	6226(4)	2800(3)	8139(3)	13(1)
C(33)	4475(4)	4039(3)	8600(2)	12(1)
C(34)	7150(4)	4403(4)	7488(3)	17(1)
I(1)	-1468(1)	1453(1)	6680(1)	19(1)
Cl(1)	-1166(1)	1459	6725	19(1)



Solid-state structure of [**2r**][$\mathrm{SbF_6}$] with thermal ellipsoids rendered at the 50% probability level and with hydrogen atoms, disorder, and [$\mathrm{SbF_6}$]$^-$ counterion omitted for clarity.

Crystallographic Data for [**2r**][$\mathrm{SbF_6}$].

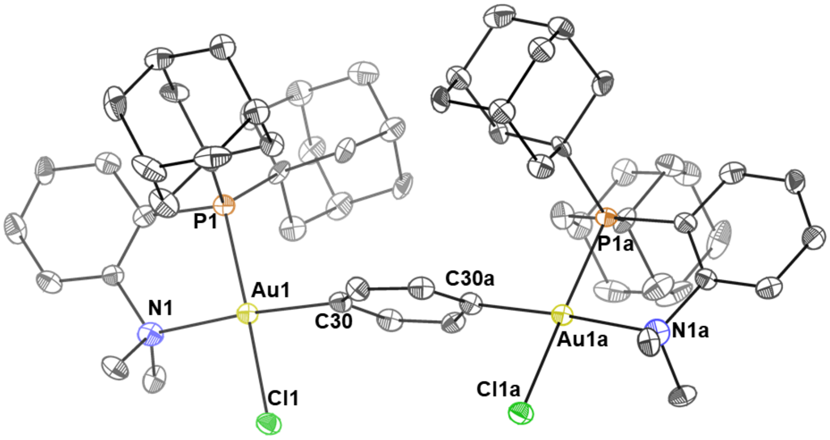
Identification code	JS-17	
CCDC Code	1835366	
Empirical formula	C45 H49 Au Cl0.85 F6 I0.15 N O P Sb	
Formula weight	1132.70	
Temperature	100.0 K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	*P*-1	
Unit cell dimensions	*a* = 10.0424(11) Å	α = 101.463(3)°
	b = 12.0230(13) Å	β = 101.135(3)°
	c = 19.663(2) Å	γ = 100.103(3)°
Volume	2225.8(4) Å^3	
Z	2	
Density (calculated)	1.690 Mg/m^3	
Absorption coefficient	4.149 mm^{-1}	
F(000)	1111	
Crystal size	0.25 x 0.22 x 0.18 mm^3	
Theta range for data collection	1.773 to 26.452°.	
Index ranges	$-12 \leq h \leq 12$, $-15 \leq k \leq 15$, $-24 \leq l \leq 24$	
Reflections collected	61519	
Independent reflections	9174 [*R*(int) = 0.0487]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.6465 and 0.5276	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9174 / 0 / 526	
Goodness-of-fit on F^2	1.114	
Final *R* indices [$I \leq 2\sigma(I)$]	*R*1 = 0.0460, w*R*2 = 0.0956	

R indices (all data)	*R*1 = 0.0624, w*R*2 = 0.1054
Extinction coefficient	n/a
Largest diff. peak and hole	2.770 and -3.305 e.Å^{-3}

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for [**2r**][SbF_6]. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Au(1)	8747(1)	8127(1)	2346(1)	28(1)
Sb(1)	8659(1)	2683(1)	819(1)	54(1)
P(1)	6451(2)	8178(1)	1870(1)	17(1)
Cl(1)	11102(3)	8142(3)	2743(3)	39(1)
F(6)	7153(5)	3379(4)	666(3)	58(1)
F(3)	8074(5)	1772(4)	-108(3)	60(1)
F(5)	9733(5)	3803(5)	500(3)	71(2)
C(19)	5165(6)	6772(5)	1714(3)	21(1)
F(2)	10188(7)	2025(9)	993(4)	132(4)
O(1)	8334(7)	4433(4)	5181(3)	57(2)
C(10)	5593(6)	9333(5)	3041(3)	22(1)
C(29)	8585(6)	7911(5)	3334(4)	26(1)
C(25)	2690(6)	5642(5)	1247(4)	28(2)
N(1)	9124(6)	8318(5)	1318(3)	33(1)
F(4)	7577(7)	1522(8)	1114(4)	116(3)
C(8)	6625(7)	8400(5)	996(3)	27(1)
C(26)	3666(6)	6845(5)	1394(4)	24(1)
C(9)	6024(6)	9523(5)	2354(3)	21(1)
C(20)	5621(6)	5870(5)	1177(4)	24(1)
C(24)	2739(7)	5250(6)	1944(4)	35(2)
C(21)	4626(7)	4674(5)	1033(4)	28(2)
C(16)	7392(6)	10480(5)	2543(3)	22(1)
C(15)	7175(6)	11617(5)	2977(4)	25(1)
C(27)	5209(7)	6372(5)	2411(3)	27(1)
C(28)	3156(7)	4763(5)	713(4)	31(2)
C(32)	8622(6)	7682(5)	4742(4)	28(1)
C(30)	8688(6)	8862(5)	3878(4)	30(2)
C(11)	5428(7)	10496(5)	3480(4)	31(2)
C(39)	8451(8)	5404(6)	5061(4)	43(2)
C(3)	7910(8)	8446(5)	818(4)	33(2)
C(31)	8686(6)	8740(5)	4566(4)	28(1)

C(34)	8756(7)	8489(6)	6047(4)	33(2)
C(44)	8561(6)	6802(5)	3486(4)	31(2)
C(22)	4683(7)	4289(5)	1727(4)	36(2)
C(38)	8564(8)	6450(6)	5629(5)	42(2)
C(33)	8649(7)	7551(6)	5473(4)	32(2)
C(43)	8565(7)	5800(5)	2969(4)	32(2)
C(7)	5496(7)	8497(5)	486(4)	30(2)
C(14)	6004(7)	12027(5)	2529(4)	31(2)
C(45)	8542(7)	6691(5)	4189(4)	30(2)
C(23)	4221(7)	5165(6)	2258(4)	34(2)
C(18)	6793(7)	11411(5)	3662(4)	28(2)
C(35)	8806(7)	8353(7)	6728(4)	38(2)
C(40)	8472(8)	5570(6)	4342(4)	38(2)
C(17)	4875(7)	9952(5)	1904(4)	28(1)
C(42)	8487(8)	4736(6)	3125(4)	40(2)
C(13)	4661(7)	11085(5)	2347(4)	34(2)
C(6)	5642(10)	8650(6)	-176(4)	44(2)
C(12)	4274(7)	10898(6)	3037(4)	38(2)
C(4)	8047(9)	8599(6)	150(4)	43(2)
C(5)	6930(11)	8712(6)	-340(4)	53(3)
C(2)	10305(8)	9355(7)	1426(4)	47(2)
C(41)	8437(8)	4627(6)	3807(4)	42(2)
C(36)	8737(8)	7278(7)	6876(4)	45(2)
F(1)	9258(7)	3616(12)	1740(3)	171(5)
C(37)	8610(8)	6327(7)	6324(5)	45(2)
C(1)	9561(8)	7223(6)	1016(5)	49(2)
I(1)	11428(5)	8134(4)	3083(3)	36(2)



Solid-state structure of [**2s**][SbF$_6$]$_2$ with thermal ellipsoids rendered at the 50% probability level and with hydrogen atoms, one co-crystallized DCM molecule and two [SbF$_6$]$^-$ counterions omitted for clarity.

Crystallographic Data for [**2s**][SbF$_6$]$_2$·DCM.

Identification code	JS-03	
CCDC Code	1835365	
Empirical formula	C64 H88 Au2 Cl6 F12 N2 P2 Sb2	
Formula weight	2025.43	
Temperature	100.0 K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	*Pccn*	
Unit cell dimensions	*a* = 20.8838(10) Å	α = 90°
	b = 17.9885(10) Å	β = 90°
	c = 18.4736(10) Å	γ = 90°
Volume	6939.9(6) Å^3	
Z	4	
Density (calculated)	1.939 Mg/m^3	
Absorption coefficient	5.336 mm^{-1}	
F(000)	3944	
Crystal size	0.22 x 0.08 x 0.05 mm^3	
Theta range for data collection	1.857 to 24.998°.	
Index ranges	$-24 \le h \le 24$, $-21 \le k \le 21$, $-21 \le l \le 21$	
Reflections collected	36322	
Independent reflections	6107 [*R*(int) = 0.1193]	
Completeness to theta = 24.998°	99.9%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7452 and 0.4798	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6107 / 0 / 396	
Goodness-of-fit on F^2	1.059	
Final *R* indices [$I > \sigma(I)$]	*R*1 = 0.0468, w*R*2 = 0.1034	

R indices (all data)	$R1 = 0.0913$, $wR2 = 0.1292$
Extinction coefficient	n/a
Largest diff. peak and hole	2.319 and -2.320 e.Å^{-3}

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for [**2s**][SbF_6]$_2$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Au(1)	2084(1)	5662(1)	4609(1)	18(1)
Sb(1)	3955(1)	3336(1)	3471(1)	27(1)
Cl(1)	1940(1)	6015(1)	3399(1)	27(1)
P(1)	2190(1)	5276(1)	5803(1)	18(1)
Cl(3)	5138(1)	2465(2)	523(2)	49(1)
Cl(2)	4936(2)	4028(2)	835(2)	58(1)
F(2)	3431(3)	3244(3)	4286(3)	30(1)
F(6)	3227(3)	3496(4)	2901(3)	44(2)
F(5)	4476(3)	3436(4)	2652(3)	48(2)
F(1)	4011(3)	4360(3)	3638(3)	46(2)
F(4)	3887(3)	2315(3)	3295(4)	48(2)
F(3)	4666(3)	3165(4)	4065(4)	50(2)
N(1)	1760(4)	4539(5)	4385(4)	25(2)
C(30)	2346(5)	6740(5)	4739(5)	21(2)
C(28)	1955(4)	6579(5)	6623(5)	21(2)
C(32)	3136(5)	7723(6)	4726(5)	22(2)
C(3)	1742(5)	4038(5)	5038(5)	20(2)
C(31)	2985(5)	6982(6)	4704(5)	23(2)
C(23)	1481(5)	7052(6)	7056(5)	26(2)
C(27)	377(5)	6040(6)	7094(5)	28(2)
C(4)	1600(5)	3300(6)	4949(6)	26(2)
C(19)	1641(4)	5819(5)	6404(5)	17(2)
C(8)	1876(4)	4345(5)	5708(5)	20(2)
C(26)	1030(5)	5976(6)	5963(5)	25(2)
C(7)	1822(5)	3858(6)	6307(5)	24(2)
C(24)	883(5)	7177(5)	6597(6)	28(3)
C(2)	2216(5)	4219(6)	3823(5)	27(3)
C(25)	557(5)	6437(6)	6411(6)	28(2)
C(14)	4212(5)	5295(6)	6983(5)	26(2)
C(20)	1451(5)	5402(6)	7106(5)	27(3)
C(21)	983(5)	5894(6)	7555(6)	30(3)

C(6)	1672(5)	3126(6)	6211(6)	28(3)
C(17)	3142(5)	4686(6)	6761(5)	27(2)
C(22)	1296(5)	6637(6)	7741(6)	34(3)
C(1)	1107(4)	4566(5)	4070(6)	25(2)
C(15)	4125(5)	5747(6)	6296(5)	26(2)
C(9)	3050(4)	5142(5)	6056(5)	22(2)
C(5)	1560(5)	2843(6)	5549(6)	31(3)
C(29)	4401(5)	5326(7)	5649(5)	34(3)
C(10)	3355(5)	4712(7)	5413(6)	34(3)
C(18)	3861(5)	4550(6)	6906(6)	28(3)
C(11)	4070(5)	4582(7)	5570(6)	36(3)
C(16)	3397(5)	5884(6)	6167(6)	26(2)
C(33)	5175(6)	3166(6)	1186(6)	40(3)
C(12)	4147(5)	4129(6)	6261(6)	40(3)

VI. References

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