Electronic Supplementary Material (ESI) for Green Chemistry.
This journal is © The Royal Society of Chemistry 2020

Mechanochemical Synthesis of (Hetero)Aryl Au(I) Complexes

Supporting Information

Index

Index **2**
General Remarks **3**
Transmetalation from boronic acids **5**
General procedure for spectroscopic yields in Table 1 and Scheme 1 (Procedure A1) 5
General procedure for isolated yields in Scheme 1 (Procedure A2) 5
Synthesis and characterization of aryl complexes **2a**–**i**,**k**,**l** (Scheme 1) 6
C–H Auration of (hetero)arenes **11**
General procedure for spectroscopic yields in Table 2 (Procedure B1) 11
General procedure for isolated yields in Schemes 2 and 3 (Procedure B2) 11
Synthesis and characterization of haloaryl complexes **3a**–**g** (Scheme 2) 12
Synthesis and characterization of heteroaryl complexes 4a–e (Scheme 3) **14**
Synthesis and characterization of NHC complexes 5a–e (Scheme 4) **16**
Synthesis and Characterization of complexes in Figure 2 ..... **18**
C–H auration mechanistic studies (Schemes 5–7) **20**
Experimental procedure for Scheme 5 20
Experimental procedure for Scheme 6 20
Preparation and characterization of **S4** 21
Procedure for solution-phase aryl exchange experiments (Scheme S1) 22
Procedure for Scheme 7 23
Computational details **25**
Crystallographic data **31**
References **36**
NMR Spectra **37**

General Remarks

^{1}H, ^{13}C, ^{19}F and ^{31}P NMR spectra were recorded on an Agilent MR400-DD2 spectrometer (^{1}H: 399.97 MHz, ^{13}C: 100.58 MHz, ^{19}F: 376.32 MHz, ^{31}P: 161.92 MHz) or on a Bruker Avance Neo (TXO) spectrometer (^{1}H: 500.16 MHz, ^{13}C: 125.78 MHz) at room temperature (25 °C). ^{1}H and ^{13}C shifts were referenced indirectly to tetramethylsilane using the residual solvent peaks of DMSO-d_6 (^{1}H: 2.50 ppm, ^{13}C: 39.52 ppm), C_6D_6 (^{1}H: 7.16 ppm, ^{13}C: 128.06 ppm) and $CDCl_3$ (^{1}H: 7.26 ppm, ^{13}C: 77.16 ppm). ^{19}F, and ^{31}P chemical shifts were referenced based on instrument calibration with an external standard (^{19}F: $CFCl_3$, ^{31}P: 85% H_3PO_4 (aq)). Unless otherwise stated, ^{31}P spectra was recorded with ^{1}H decoupling. ^{1}H and ^{31}P NMR spectra used for quantification was recorded with 30 s relaxation delay and 32 scans (or equivalent to afford S/N > 250:1). Chemical shifts are reported in ppm and coupling constants (J) in Hz. Peak multiplicities are abbreviated as follows: s (singlet), d (doublet), t (triplet), appt (apparent triplet), q (quartet), hept (heptet) and m (multiplet).

Unless otherwise stated, all reagents were obtained commercially and used without further purification. Ethanol (99.5%, analytical grade) was purchased from Solveco. KOH (100%, Honeywell) was ground from pellets with mortar and pestle into a fine powder and used immediately. Deionized water was used for all reactions and purifications.

Phenyl-, 3-tolyl-, 4-methoxyphenyl-, 4-styrenyl-, and 3-thiophenylboronic acid were recrystallized from hot water and stored at –22 °C prior to use. 2-Methoxyphenyl-, 4-chlorophenyl-, 4-iodophenyl-, and 4-(trifluoromethyl)phenylboronic acid were recrystallized from hot water and a minimal amount of DMSO and stored at –22 °C prior to use. 9-Phenyl-9*H*-carbazol-3-yl boronic acid was suspended in a mixture of hot water and DMSO for approximately 1 h. The hot suspension was vacuum-filtered, the filtrate was allowed to cool to ambient temperature, and the precipitated boronic acid was collected by vacuum filtration and stored –22 °C prior to use.

3-Tolyl potassium 2-hydroxymethyl-2-methylpropane-1,3-diol trialkoxyborate was prepared according to a literature procedure.[1]

Thin layer chromatography (TLC) was carried out using aluminium-backed plates coated with Silica gel 60 (0.20 mm, UV 254) and visualized under ultraviolet light (λ = 254 nm) or by thermal decomposition. Purification by column chromatography was performed using Silica gel 60 H (particle size 0.063-0.100 mm).

High resolution mass spectrometry: High-resolution electrospray ionisation mass spectrometry was performed on a Thermo Scientific LTQ Orbitrap velos pro instrument, or on a micrOTOF II Focus instrument (Bruker Daltonics, Coventry, UK). High-resolution nanospray ionisation was performed on a Synapt G2S instrument (Waters, Manchester, UK) using a Triversa chip based nanospray source (Advion Biosciences, Norwich, UK).

X-ray crystallography: Single crystals of **3d** and **3f** suitable for X-ray diffraction analysis were obtained by recrystallization from layered CH_2Cl_2/pentane in a 5 mm diameter NMR tube at ambient temperature in the dark. All the measurements performed using graphite-monochromatized MoKα radiation at 170K using a Bruker D8 APEX-II equipped with a CCD camera. Data reduction was performed with SAINT[2] and CrysAlisPro (Rigaku OD). Absorption corrections for the area detector were performed using SADABS.[3] The structure was solved by direct methods and refined by full-matrix least-squares techniques against F2 using all data (SHELXT and SHELXL)[4] implemented in OLEX2.[5] All non-hydrogen atoms were refined with anisotropic displacement parameters if not stated otherwise in the cif files. Hydrogen atoms constrained in geometric positions to their parent atoms.

Milling details: All milling reactions were conducted using an InSolido Techologies IST 636 High Energy Mixer Mill in Teflon™ (PTFE) vessels (14 mL inner volume) from InSolido Techologies and using stainless steel balls (15 mm diameter) weighing 13.6 g (Figure S1).

Figure S1. InSolido Technologies IST 636 High Energy Mixer Mill (top); Teflon™ vessels and stainless steel milling ball (bottom).

Transmetalation from boronic acids

General procedure for spectroscopic yields in Table 1 and Scheme 1 (Procedure A1)

R_3PAuCl (0.10 mmol, 1.0 equiv.), boronic acid (0.10 mmol, 1.0 equiv.) and additives (KOH powder (0.12 mmol, 1.2 equiv.) and H_2O (0.10 mL) for entries in Scheme 1) were added to a 14 mL Teflon™ vessel together with one stainless steel ball (15 mm diameter, 13.6 g). The vessel was sealed and subjected to milling for 1 h at 30 Hz. The reaction mixture was extracted with CH_2Cl_2* (2 x 5 mL); the combined extractions were washed with H_2O (20 mL), and the aqueous layer was extracted with CH_2Cl_2* (2 x 10 mL). The organic layers were combined and dried over Na_2SO_4. Solids were removed by vacuum filtration, and the filtrate was concentrated to dryness *in vacuo*. Product yield were determined by ^{31}P NMR spectroscopy (d1 = 30 s; S/N > 250:1) based on ratios of signal integration for starting R_3PAuCl and product peaks.

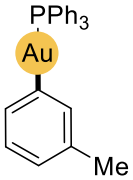
*CH_2Cl_2 was used only to ensure full recovery of $R_3PAu(I)$ species for accurate quantification as part of the method development. It was substituted by EtOAc in subsequent experiments for actual product isolation (*vide infra*).

General procedure for isolated yields in Scheme 1 (Procedure A2)

R_3PAuCl (0.10 mmol, 1.0 equiv.) and boronic acid (0.12 mmol, 1.2 equiv.) were added to a 14 mL Teflon™ vessel. KOH was added as a stock solution (1.25 M (aq), 0.12 mL, 0.15 mmol, 1.5 equiv.) together with one stainless steel ball (15 mm diameter, 13.6 g). The vessel was sealed and subjected to milling for 1 h at 30 Hz. The reaction mixture was extracted with EtOAc (4 x 5 mL). The stainless steel ball was briefly sonicated in EtOAc (5 mL) to extract adsorbed material. The combined organic fractions were washed with H_2O (20 mL), and the aqueous layer was extracted with EtOAc (2 x 10 mL). The organic layers were combined and dried over Na_2SO_4. Solids were removed by vacuum filtration and the filtrate was concentrated *in vacuo*. The resulting residue was re-dissolved in a minimal amount of EtOAc and filtered through a tightly packed plug of Celite. Unless otherwise stated, the filtrate was concentrated to dryness *in vacuo* to afford analytically pure product.

Synthesis and characterization of aryl complexes **2a**–**i**,**k**,**l** (Scheme 1)

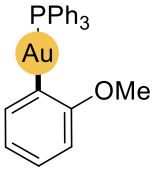
3-Tolyl(triphenylphosphine)gold(I) (2a)[1]



Procedure A1 afforded **2a** in >99% spectroscopic yield.

Procedure A2 afforded isolated **2a** as a colourless solid (50 mg, 93%). Spectral data accord with previously reported values.

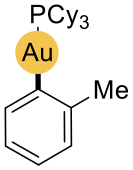
2-Methoxyphenyl(triphenylphosphine)gold(I) (2b)[6]



Procedure A1 afforded **2b** in >99% spectroscopic yield.

Procedure A2 afforded isolated **2b** as a colourless solid (48 mg, 86%). Spectral data accord with previously reported values.

2-Methylphenyl(tricyclohexylphosphine)gold(I) (2c)[7]

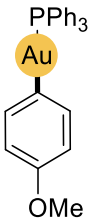


A modified version of procedure A1 using 2.0 equiv. KOH powder afforded **2c** in 90% spectroscopic yield.

A modified version of Procedure A2 using 3.0 equiv. KOH (2.5 M (aq), 0.12 mL) with milling at 25 Hz afforded **2c** as a colourless solid (51 mg, 86%). Spectral data accord with previously reported values.

^{1}H and ^{31}P NMR characterization data for spectroscopic yield determination in $CDCl_3$: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46–7.38 (m, 1H), 7.18 (d, *J* = 7.3 Hz, 1H), 7.10 (dd, *J* = 7.4, 7.3 Hz, 1H), 6.98 (dd, *J* = 7.4, 7.4 Hz, 1H), 2.54 (s, 3H), 2.12–1.95 (m, 8H), 1.92–1.82 (m, 7H), 1.80–1.68 (m, 3H), 1.60–1.49 (m, 5H), 1.39–1.17 (m, 10H); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 57.4.

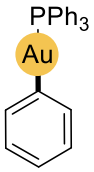
4-Methoxyphenyl(triphenylphosphine)gold(I) (2d)[8]



Procedure A1 afforded **2d** in 92% spectroscopic yield.

A modified version of Procedure A2 using 1.4 equiv. Ar-$B(OH)_2$ afforded **2d** as a colourless solid (55 mg, 97%). Spectral data accord with previously reported values.

Phenyl(triphenylphosphine)gold(I) (2e)[9]

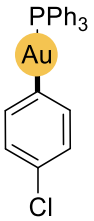


Procedure A1 afforded **2e** in >99% spectroscopic yield.

Procedure A2 afforded isolated **2e** as a colourless solid (50 mg, 94%). Spectral data accord with previously reported values.

^{1}H and ^{31}P NMR characterization data for spectroscopic yield determination in $CDCl_3$: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.7–7.5 (m, 8H), 7.5–7.4 (m, 9H), 7.3 (appt, *J* = 7.6 Hz, 2H), 7.1 (m, 1H); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 43.5.

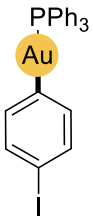
4-Chlorophenyl(triphenylphosphine)gold(I) (2f)[1]



Procedure A1 afforded **2f** in 86% spectroscopic yield.

Procedure A2 afforded isolated **2f** as a colourless solid (55 mg, 97%). Spectral data accord with previously reported values.

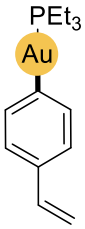
4-Iodophenyl(triphenylphosphine)gold(I) (2g)[1]



Procedure A1 afforded **2g** in 83% spectroscopic yield.

An isolated sample of **2g** was prepared by a modified version of Procedure A2: 2.5 equiv. KOH (2.5 M (aq), 0.10 mL) was used and milling was conducted at 25 Hz for 2 h. After Celite plug filtration, volatiles were removed *in vacuo*, and the resulting solid residue was washed with a minimal amount of EtOAc. Residual solvent was removed *in vacuo* to afford **2g** as a colourless solid (58 mg, 87%). Spectral data accord with previously reported values.

4-Vinylphenyl(triethylphosphine)gold(I) (2h)[10]

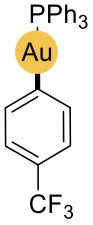


A modified version of procedure A1 using 2.0 equiv. KOH powder afforded **2h** in 93% spectroscopic yield.

An isolated sample of **2h** was prepared by a modified version of Procedure A2: 3.0 equiv. KOH (2.5 M (aq), 0.10 mL) were used and milling was conducted at 25 Hz. After Na_2SO_4 drying, filtration and evaporation, the residue was dissolved in a minimal amount of pentane and filtered through a tightly packed Celite plug and solvent removed *in vacuo* to afford **2h** as a brown oil (39 mg, 93%) Spectral data accord with previously reported values.

^{1}H and ^{31}P NMR characterization data for spectroscopic yield determination in $CDCl_3$: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 (dd, $J_{H\text{-}H}$ = 7.7, $J_{P\text{-}H}$ = 4.3 Hz, 2H), 7.31 (d, $J_{H\text{-}H}$ = 7.7 Hz, 2H), 6.67 (dd, $J_{H\text{-}H}$ = 17.6, 10.9 Hz, 1H), 5.67 (d, $J_{H\text{-}H}$ = 17.6 Hz, 1H), 5.09 (d, $J_{H\text{-}H}$ = 10.9 Hz, 1H), 1.82 (dq, $J_{P\text{-}H}$ = 7.9 Hz, $J_{H\text{-}H}$ = 7.9 Hz, 6H), 1.23 (dt, $J_{P\text{-}H}$ = 16.2, $J_{H\text{-}H}$ = 8.7 Hz, 9H); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 40.7.

[(4-Trifluoromethyl)phenyl](triphenylphosphine)gold(I) (2i)[9]

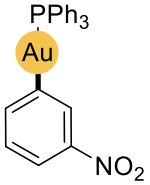


Procedure A1 afforded **2i** in >99% spectroscopic yield.

An isolated sample of **2i** was prepared by a modified version of Procedure A2: after Celite plug filtration and evaporation, the resulting solid residue was washed with pentane (4 x 1 mL) to afford **2i** as a brown solid (51 mg, 84%). Spectral data accord with previously reported values.

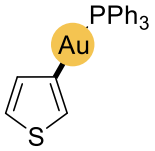
^{1}H and ^{31}P NMR characterization data for spectroscopic yield determination in $CDCl_3$: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.7–7.6 (m, 2H), 7.6–7.6 (m, 6H), 7.6–7.4 (m, 11H); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 43.2.

3-Nitrophenyl(triphenylphosphine)gold(I) (2j)[11]



Procedure A1 afforded **2j** in 23% spectroscopic yield. Spectral data accord with previously reported values.

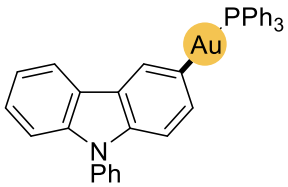
3-Thiophenyl(triphenylphosphine)gold(I) (2k)[1]



Procedure A1 afforded **2k** in >99% spectroscopic yield.

Procedure A2 afforded isolated **2k** as a colourless solid (52 mg, 96%). Spectral data accord with previously reported values.

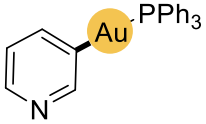
(9-Phenyl-9*H*-carbazol-3yl)(triphenylphosphine)gold(I) (2l)[1]



A modified version of procedure A1 using 2.0 equiv. KOH powder afforded **2l** in >99% spectroscopic yield.

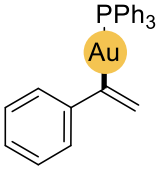
An isolated sample of **2l** was prepared by a modified version of Procedure A2: 1.4 equiv. Ar-$B(OH)_2$ and 3.0 equiv. KOH (2.5 M (aq), 0.10 mL) were used and milling was conducted at 36 Hz. After Na_2SO_4 drying, filtration and evaporation, the resulting solid residue was washed 3x with a minimal amount of EtOAc. Residual solvent was removed *in vacuo* to afford **2l** as a colourless solid (44 mg, 63%). Spectral data accord with previously reported values.

(3-Pyridyl)(triphenylphosphine)gold(I) (2m)



Procedure A1 afforded **2m** in trace amounts (spectroscopic).

[(1-Vinyl)phenyl](triphenylphosphine)gold(I) (2n)[1]



Procedure A1 afforded **2n** in 22% spectroscopic yield. Spectral data accord with previously reported values.

C–H Auration of (hetero)arenes

General procedure for spectroscopic yields in Table 2 (Procedure B1)

R_3PAuCl (0.10 mmol, 1.0 equiv.), arene and base were added to a 14 mL Teflon™ vessel together with one stainless steel ball (15 mm diameter, 13.6 g). The vessel was sealed and subjected to milling for 1 h at 30 Hz. The reaction mixture was extracted with CH_2Cl_2* (2 x 5 mL); the combined extractions were washed with H_2O (20 mL), and the aqueous layer was extracted with CH_2Cl_2* (2 x 10 mL). The organic layers were combined and dried over Na_2SO_4. Solids were removed by vacuum filtration, and the filtrate was concentrated to dryness *in vacuo*. Product yield was determined by ^{31}P NMR spectroscopy (d1 = 30 s; S/N > 250:1) based on ratios of signal integration for starting R_3PAuCl and product peaks.

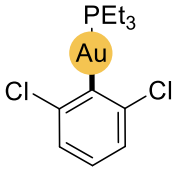
*CH_2Cl_2 was used only to ensure full recovery of $R_3PAu(I)$ species for accurate quantification as part of the method development. It was substituted by EtOAc in subsequent experiments for actual product isolation (*vide infra*).

General procedure for isolated yields in Schemes 2 and 3 (Procedure B2)

R_3PAuCl (0.10 mmol, 1.0 equiv.), arene (4.0 equiv.) and base (4.0 equiv.; KO^{t}Bu powder for entries in Scheme 2, KOH powder for entries in Scheme 3) were added to a 14 mL Teflon™ vessel together with one stainless steel ball (15 mm diameter, 13.6 g). The vessel was sealed and subjected to milling for 1 h at 30 Hz. The reaction mixture was extracted with EtOAc (4 x 5 mL); the combined extractions were washed with H_2O (20 mL), and the aqueous layer was extracted with EtOAc (2 x 10 mL). The organic layers were combined and dried over Na_2SO_4. Solids were removed by vacuum filtration and the filtrate was concentrated *in vacuo*. Additional purification was performed as necessary (see individual entries for details).

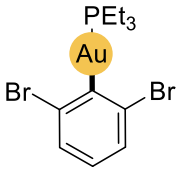
Synthesis and characterization of haloaryl complexes **3a–g** (Scheme 2)

2,6-Dichlorophenyl(triethylphosphine)gold(I) (3a)[12]



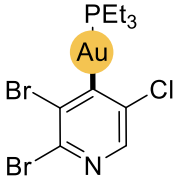
A modified version of Procedure B2 with milling conducted for 1.5 h afforded **3a** as a colourless oil (42 mg, 92%) after filtration of the dried EtOAc extractions through a short silica gel pad. Spectral data accord with previously reported values.

2,6-Dibromophenyl(triethylphosphine)gold(I) (3b)[12]



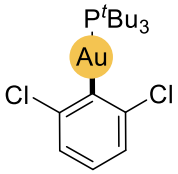
A modified version of Procedure B2 with milling conducted for 1.5 h afforded **3b** as a colourless oil (50 mg, 91%) after filtration of the dried EtOAc extractions through a short silica gel pad. Spectral data accord with previously reported values.

(2,3-dibromo-5-chloropyridin-4-yl)(triethylphosphine)gold(I) (3c)



An isolated sample of **3c** was prepared by a modified version of Procedure B2: after Celite plug filtration and evaporation, the resulting residue was washed 3x with a minimal amount of pentane. Residual solvent was removed *in vacuo* to afford **3c** as a yellow solid (41 mg, 70%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.19 (d, $J_{H\text{-}P}$ = 1.9 Hz, 1H), 1.87 (dq, $J_{H\text{-}P}$ = 9.5, $J_{H\text{-}H}$ 7.6 Hz, 6H), 1.28 (dt, $J_{H\text{-}P}$ = 18.1, $J_{H\text{-}H}$ = 7.6 Hz, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.8 (d, $J_{C\text{-}P}$ = 4 Hz), 141.0 (d, $J_{C\text{-}P}$ = 7 Hz), 139.6 (d, $J_{C\text{-}P}$ = 4 Hz), 133.8 (d, $J_{C\text{-}P}$ = 4 Hz), 18.2 (d, $J_{C\text{-}P}$ = 32 Hz), 9.3, Au*C* not observed; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 36.9; **HRMS** (ES+) calcd. for $C_{11}H_{17}AuBr_2ClNP$ $[M+H]^+$: 583.8819 found 583.8837

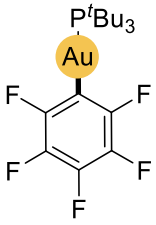
2,6-Dichlorophenyl(tri-*tert*-butylphosphine)gold(I) (3d)



A modified version of Procedure B2 with milling conducted for 2 h at 36 Hz afforded **3d** as a colourless solid (50 mg, 91%). **^{1}H NMR** (400 MHz, C_6D_6) δ 7.35 (dd, $J_{H\text{-}H}$ = 7.9, $J_{H\text{-}P}$ = 1.5 Hz, 2H), 6.64

(dd, $J_{H\text{-}H}$ = 7.9, 7.9 Hz, 1H), 1.21 (d, $J_{H\text{-}P}$ = 12.9 Hz, 27H); **^{13}C NMR** (101 MHz, C_6D_6) δ 174.6 (d, *J* = 100 Hz), 144.3 (d, *J* = 4 Hz), 127.7, 126.3 (d, *J* = 4 Hz), 39.0 (d, *J* = 16 Hz), 32.2 (d, *J* = 5 Hz); **^{31}P NMR** (162 MHz, C_6D_6) δ 90.4; **HRMS** (ES+) calcd. for $C_{30}H_{57}Au_2Cl_2P_2$ $[M+AuP^tBu_3]^+$: 943.2644 found 943.2673

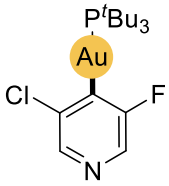
Pentafluorophenyl(tri-*tert*-butylphosphine)gold(I) (3e)[12]



Procedure B2 afforded isolated **3e** as a colourless microcrystalline solid (50 mg, 89%). Spectral data accord with previously reported values.

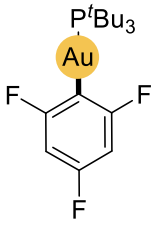
A repeat of this procedure on 0.5 mmol scale afforded 230 mg (81%) of product.

(3-chloro-5-fluoropyridin-4-yl)(tri-*tert*-butylphosphine)gold(I) (3f)



An isolated sample of **3f** was prepared by a modified version of Procedure B2: after filtration and concentration of the dried EtOAc extractions, silica gel chromatography (pentane/EtOAc 10:1) afforded **3f** as a colourless solid (46 mg, 90%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.33 (dd, $J_{H\text{-}F}$ = 2.6 Hz, $J_{H\text{-}H}$ = 1.6 Hz, 1H), 8.23 (dd, $J_{H\text{-}F}$ = 2.6 Hz, $J_{H\text{-}H}$ = 1.6 Hz, 1H), 1.56 (d, $J_{H\text{-}P}$ = 13.2 Hz, 27H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.23 (dd, $J_{C\text{-}P}$ = 95, $J_{C\text{-}F}$ = 58 Hz), 163.97 (dd, $J_{C\text{-}F}$ = 241, $J_{C\text{-}P}$ = 3 Hz), 142.94 (dd, $J_{C\text{-}P}$ = $J_{C\text{-}F}$ = 3 Hz), 141.45 (dd, $J_{C\text{-}P}$ = 17, $J_{C\text{-}F}$ = 4 Hz), 133.31 (dd, $J_{C\text{-}F}$ = 34, $J_{C\text{-}P}$ = 3 Hz), 39.37 (d, $J_{C\text{-}P}$ = 16 Hz), 32.45 (d, $J_{C\text{-}P}$ = 5 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ –104.08 (ddd, $J_{F\text{-}P}$ = 6.2 Hz, $J_{F\text{-}H}$ = 2.6, 2.6 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 91.2 (d, $J_{P\text{-}F}$ = 6.2 Hz); **HRMS** (ES+) calcd. for $C_{17}H_{30}AuClFNP$ $[M+H]^+$: 530.1448 found 530.1425

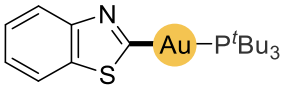
2,4,6-trifluorophenyl(tri-*tert*-butylphosphine)gold(I) (3g)[12]



Procedure B2 afforded isolated **3g** as a colourless microcrystalline solid (48 mg, 91%). Spectral data accord with previously reported values.

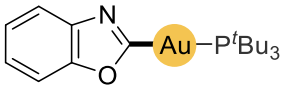
Synthesis and characterization of heteroaryl complexes 4a–e (Scheme 3)

Benzothiazol-2-yl(tri-tert-butylphosphine)gold(I) (4a)[12]



An isolated sample of **4a** was prepared by a modified version of Procedure B2: after filtration and concentration of the dried EtOAc extractions, silica gel chromatography (pentane/EtOAc 4:1) afforded **4a** as a colourless solid (45 mg, 85%). Spectral data accord with previously reported values.

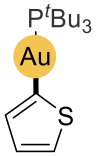
Benzoxazol-2-yl(tri-*tert*-butylphosphine)gold(I) (4b)[12]



Procedure B1 using 4.0 equiv. KOH afforded **4b** in 47% spectroscopic yield with milling conducted at 30 Hz and in 93% yield at 36 Hz.

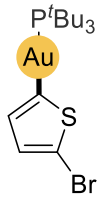
An isolated sample of **4a** was prepared by a modified version of Procedure B2: milling was conducted at 36 Hz. After filtration and concentration of the dried EtOAc extractions, silica gel chromatography (pentane/EtOAc 1:1 + 1% NEt_3) afforded **4b** as a brown solid (44 mg, 85%). Spectral data accord with previously reported values.

Thiophen-2-yl(tri-*tert*-butylphosphine)gold(I) (4c)



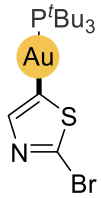
A modified version of Procedure B2 using 4.0 equiv. KO^{t}Bu and with milling conducted at 36 Hz afforded **4c** as a colourless solid (42 mg, 88%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60 (dd, $J_{H\text{-}H}$ = 4.7, $J_{H\text{-}P}$ = 1.2 Hz, 1H), 7.39 (ddd, $J_{H\text{-}H}$ = 4.8, 3.2 Hz, $J_{H\text{-}P}$ = 0.8 Hz, 1H), 7.10 (dd, $J_{H\text{-}H}$ = $J_{H\text{-}P}$ = 3.2 Hz, 1H), 1.55 (d, $J_{H\text{-}P}$ = 13.0 Hz, 27H); **^{1}H{^{31}P} NMR** (400 MHz, $CDCl_3$) δ 7.60 (d, J = 4.7 Hz, 1H), 7.39 (dd, J = 4.7, 3.2 Hz, 1H), 7.10 (d, J = 3.2 Hz, 1H), 1.55 (s, 27H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 132.4 (d, J = 10 Hz), 127.1, 126.5 (d, J = 14 Hz), 38.9 (d, J = 16 Hz), 32.4, Au*C* not observed; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 92.1; **HRMS** (ES+) calcd. for $C_{16}H_{31}AuOPS$ $[M+O+H]^+$: 499.1493 found 499.1467

5-Bromothiophen-2-yl(tri-*tert*-butylphosphine)gold(I) (4d)[12]



An isolated sample of **4d** was prepared by a modified version of Procedure B2: after filtration and concentration of the dried EtOAc extractions, the resulting residue was extracted with pentane (3 x 5 mL). Volatiles were removed *in vacuo* to afford **4d** as a colourless oil (46 mg, 82%). Spectral data accord with previously reported values.

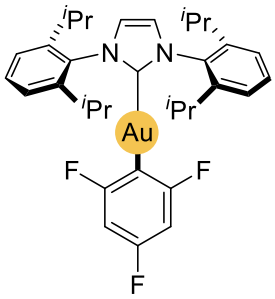
2-Bromothiazol-4-yl(tri-*tert*-butylphosphine)gold(I) (4e)[12]



An isolated sample of **4e** was prepared by a modified version of Procedure B2: milling was conducted at 36 Hz. After filtration and concentration of the dried EtOAc extractions, silica gel chromatography (30% EtOAc + 1% NEt_3 in pentane) afforded **4e** as a yellow solid (25 mg, 44%). Spectral data accord with previously reported values.

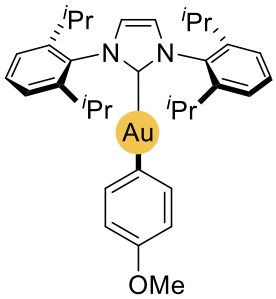
Synthesis and characterization of NHC complexes 5a–e (Scheme 4)

[N,N-Bis(2,6-diisopropylphenyl)imidazol-2-yl](2,4,6-trifluorophenyl)gold(I) (5a)[13]



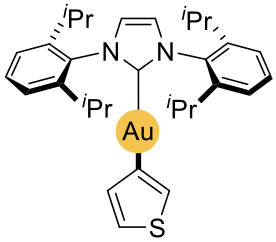
Procedure B2 using IPrAuCl (0.1 mmol) and 4.0 equiv. KO^{t}Bu afforded **5a** as a colourless solid (59 mg, 82%). Spectral data accord with previously reported values.

[1,3-Bis(2,6-diisopropylphenyl)imidazol-2-yl](4-methoxyphenyl)gold(I) (5b)[14]



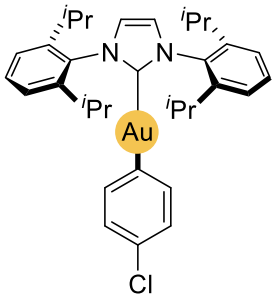
A modified version of Procedure A2 using IPrAuCl (0.1 mmol) and 1.4 equiv. Ar-B(OH)$_2$ afforded **2b** as a colourless solid (64 mg, 93%). Spectral data accord with previously reported values.

[1,3-Bis(2,6-diisopropylphenyl)imidazol-2-yl](3-thiophenyl)gold(I) (5c)[1]



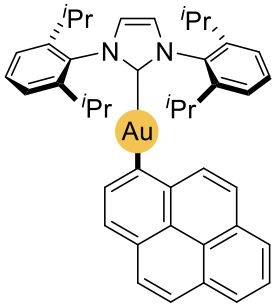
Procedure A2 using IPrAuCl (0.1 mmol) afforded isolated **5c** as a beige solid (65 mg, 98%). Spectral data accord with previously reported values.

[1,3-Bis(2,6-diisopropylphenyl)imidazol-2-yl](4-iodophenyl)gold(I) (5d)[14]



Procedure A2 using IPrAuCl (0.1 mmol) afforded isolated **5d** as a colourless solid (67 mg, 96%). Spectral data accord with previously reported values.

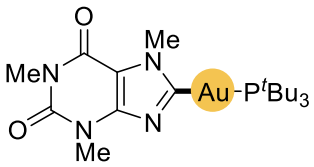
[**1,3-Bis(2,6-diisopropylphenyl)imidazol-2-yl](1-pyrenyl)gold(I) (5e)**[15]



An isolated sample of **2j** was prepared by a modified version of Procedure A2: IPrAuCl (0.1 mmol), KOH powder (0.2 mmol, 2.0 equiv.) and 0.1 mL of H_2O were used. After Na_2SO_4 drying, filtration and evaporation, silica gel chromatography (pentane/EtOAc 10:1) afforded **5e** as a colourless solid (24 mg, 31%). Spectral data accord with previously reported values.

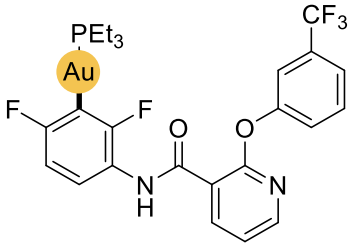
Synthesis and Characterization of complexes in Figure 2

1,3,7-trimethyl-2,6-dioxo-2,3,6,7-tetrahydropurin-8-yl(tri-*tert*-butylphosphine)gold(I) (S1)[12]



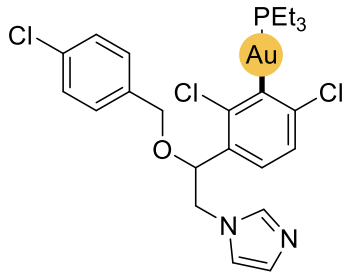
An isolated sample of **S1** was prepared by a modified version of Procedure B2 using 4.0 equiv. KOH: after EtOAc extraction, the combined organic layers were washed with H_2O (20 mL) and brine (20 mL). The aqueous layers were extracted with EtOAc (2 x 10 mL) and the combined extractions were dried over Na_2SO_4. Solids were removed by vacuum filtration, and the filtrate was concentrated *in vacuo*. The resulting residue was washed 3x with a minimal amount of ice cold EtOAc. Residual solvent was removed *in vacuo* to afford **S1** as a colourless solid (39 mg, 67%). Spectral data accord with previously reported values.

(2,6-difluoro-3-(2-(3-(trifluoromethyl)phenoxy)nicotinamido)phenyl)(triethylphosphine)gold(I) (S2)



An isolated sample of **S2** was prepared by a modified version of Procedure B2: 1.5 equiv. arene and 4.0 equiv. KO^{t}Bu were used. After filtering and concentrating the dried EtOAc extractions, silica gel chromatography (pentane/EtOAc 10:1) afforded **S2** as a colourless solid (47 mg, 66%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.90 (br s, 1H), 8.65 (dd, $J_{H\text{-}H}$ = 7.6, 2.0 Hz, 1H), 8.22–8.14 (m, 2H), 7.55–7.45 (m, 3H), 7.43–7.37 (m, 1H), 7.20–7.15 (m, 1H), 6.86–6.79 (m, 1H), 1.80 (dq, $J_{H\text{-}P}$ = 9.4 Hz, $J_{H\text{-}H}$ = 7.7 Hz, 6H), 1.18 (dt, $J_{H\text{-}P}$ = 17.9 Hz, $J_{H\text{-}H}$ = 7.7 Hz, 9H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 164.52 (ddd, $J_{C\text{-}F}$ = 230, 24 Hz, $J_{C\text{-}P}$ = 4 Hz), 160.5, 159.2, 152.6, 149.9, 142.7, 132.2 (d, J = 33 Hz), 130.1, 125.4, 122.3 (q, J = 4 Hz), 120.2, 120.0 (d, J = 8 Hz), 119.2 (q, J = 4 Hz), 117.8, 109.9 (dt, J = 32, 3 Hz), 18.0 (d, $J_{C\text{-}P}$ = 32 Hz), 9.0, (Au*C* not observed); **^{19}F NMR** (376 MHz, $CDCl_3$) δ –62.6 (s, 2F), –92.4 to –92.6 (m, 1F), –104.6 to –104.8 (m, 1F); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 40.2 (dd, $J_{P\text{-}F}$ = 8.3 Hz); **HRMS** (Nanospray) calcd. for $C_{25}H_{26}AuF_5N_2O_2P$ $[M+H]^+$: 709.1318, found 709.1326.

(2,6-dichloro-3-(1-((4-chlorobenzyl)oxy)-2-(1*H*-imidazol-1-yl)ethyl)phenyl)(triethylphosphine)-gold(I) (S3)



An isolated sample of **S3** was prepared by a modified version of Procedure B1: 0.1 mmol arene, 1.5 equiv. $(Et_3P)AuCl$ and 4.0 equiv. KO^tBu were used. The reaction mixture was extracted with CH_2Cl_2 (2 x 5 mL); the combined extractions were washed with H_2O (20 mL), and the aqueous layer was extracted with CH_2Cl_2 (2 x 10 mL). The organic layers were combined and dried over Na_2SO_4. After filtering and concentrating the dried CH_2Cl_2 extractions, silica gel chromatography (CH_2Cl_2/MeOH 20:1) afforded **S3** as a colourless semi-solid (40 mg, 57%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.54 (s, 1H), 7.31 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.28–7.26 (m, 2H), 7.11–7.04 (m, 4H), 6.96 (s, 1H), 4.96 (dd, *J* = 8.3, 2.3 Hz, 1H), 4.45 (d, *J* = 11.9 Hz, 1H), 4.21 (dd, *J* = 14.5, 2.3 Hz, 1H), 4.17 (d, *J* = 11.9 Hz, 1H), 3.98 (dd, *J* = 14.5, 8.3 Hz, 1H), 1.90 (dq, $J_{P\text{-}H}$ = 9.2, $J_{H\text{-}H}$ = 7.7 Hz, 6H), 1.32 (dt, , $J_{P\text{-}H}$ = 18.0, $J_{H\text{-}H}$ = 7.7 Hz, 9H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 174.5 (d, $J_{C\text{-}P}$ = 108 Hz), 143.4 (d, $J_{C\text{-}P}$ = 4 Hz), 141.9 (d, $J_{C\text{-}P}$ = 4 Hz), 138.0, 136.0, 133.5, 132.5 (d, $J_{C\text{-}P}$ = 4 Hz), 129.0, 129.0, 128.6, 127.0 (d, $J_{C\text{-}P}$ = 4 Hz), 125.4, 119.8, 78.5, 70.4, 51.8, 18.2 (d, $J_{C\text{-}P}$ = 31 Hz), 9.1; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 38.8; **HRMS** (ES+) calcd. for $C_{24}H_{30}AuCl_3N_2OP$ $[M+H]^+$: 695.0821, found 695.0848

C–H auration mechanistic studies (Schemes 5–7)

Experimental procedure for Scheme 5

Haloarene/heteroarene competition experiments were conducted according to a modified version of Procedure B1 using 0.1 mmol (^{t}Bu$_3$P)AuCl, 2.0 equiv. haloarene, 2.0 equiv. heteroarene, and 4.0 equiv. KO^{t}Bu. Product ratios were determined from ^{31}P NMR ($CDCl_3$) signal relative integrations.

Experimental procedure for Scheme 6

Mechanochemical aryl exchange experiments were conducted according to a modified version of Procedure B1 using 0.1 mmol (^{t}Bu$_3$P)AuAr^1, 1.0 equiv. Ar^{1}H, 2.0 equiv. Ar^{2}H, and 4.0 equiv. KO^{t}Bu.

Determination of the final ratios between complexes **3e** and **4a** by ^{31}P NMR was complicated in these cases by the formation of a side-product whose signal overlapped with that of **3e**. Complementary ^{19}F NMR analysis revealed the presence of additional fluoroaryl-containing species besides **3e**; these were subsequently identified as the known[16] compound 3-(*tert*-butyloxy)-1,2,4,5-tetrafluorobenzene and the novel C_6F_4(O^{t}Bu) complex **S4** (Figure S2; see below for preparation and characterization of an authentic sample). The integration area of the overlapping ^{31}P signals for **3e** and **S4** was thus deconvoluted by applying the ratio of the corresponding ^{19}F NMR signals, and the ^{31}P peak area for **3e** so resolved was compared to that of **4a** to give the true **3e**:**4a** ratio.

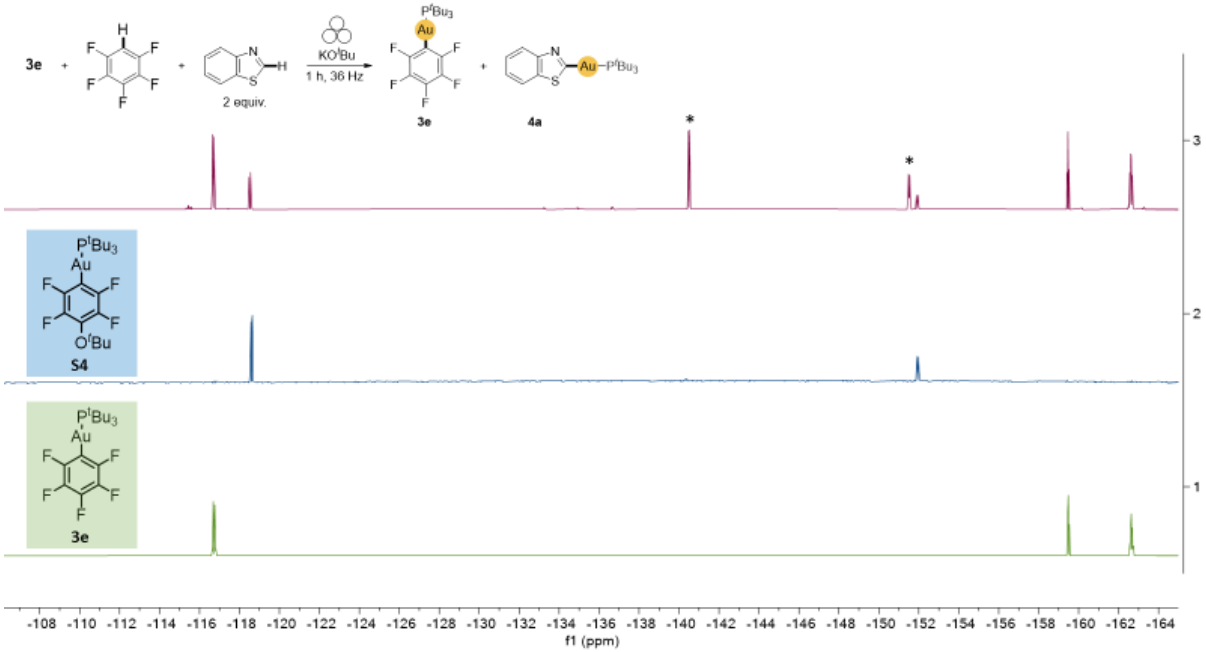
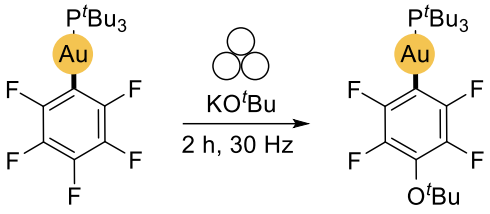


Figure S2: Comparison of the ^{19}F NMR spectrum for the aryl exchange experiment starting with **3e** with those for isolated **S4** and **3e**. Peaks in the top spectrum marked by an asterisk (*) were assigned to the additional side-product 3-(*tert*-butyloxy)-1,2,4,5-tetrafluorobenzene by comparison with previously reported chemical shifts.

Preparation and characterization of **S4**



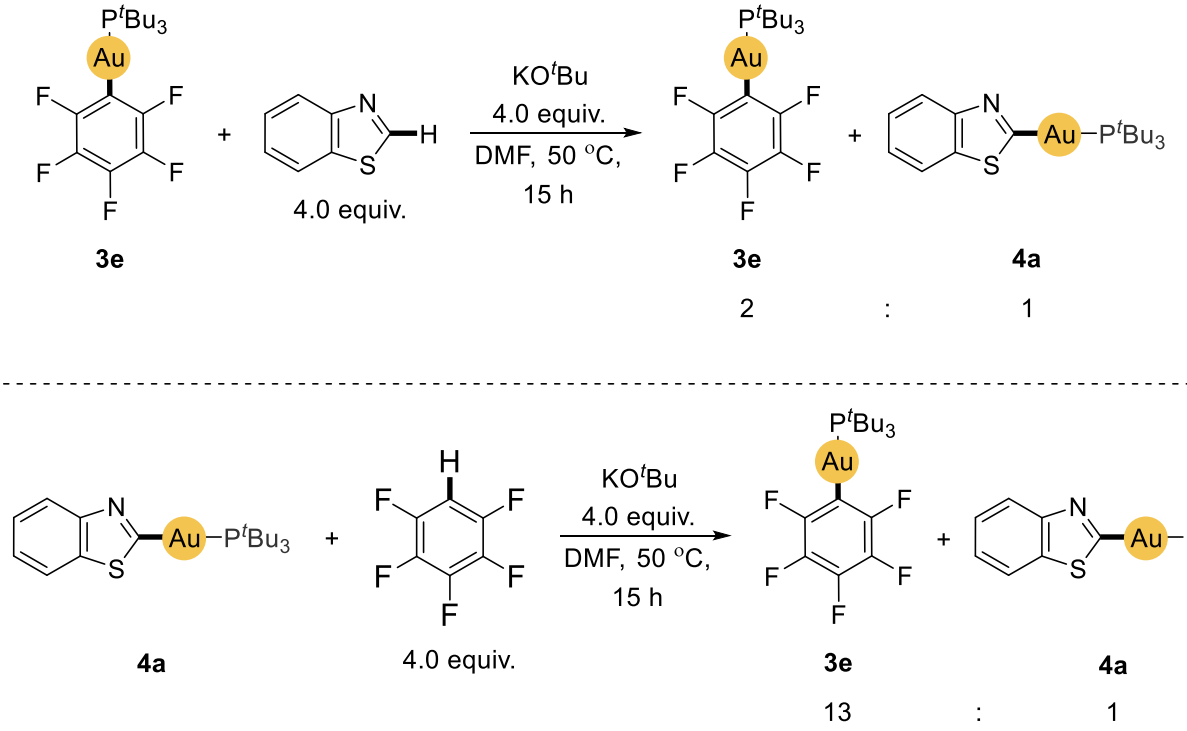
3e **S4**

(4-(tert-butoxy)-2,3,5,6-tetrafluorophenyl)(tri-tert-butylphosphine)gold(I) (S4)

Complex **3e** (57 mg, 0.1 mmol) and KO^{t}Bu (112 mg, 1.0 mmol, 10 equiv.) were added to a 14 mL Teflon™ vessel together with one stainless steel ball. The vessel was sealed and subjected to milling for 2 h at 30 Hz. The reaction mixture was extracted with CH_2Cl_2 (2 x 5 mL); the combined extractions were washed with H_2O (20 mL), and the aqueous layer was extracted with CH_2Cl_2 (2 x 10 mL). The organic layers were combined and dried over Na_2SO_4. Solids were removed by vacuum filtration, and the filtrate was concentrated to dryness *in vacuo*. The product **S4** was purified via preparative TLC (CH_2Cl_2/pentane 1:100) and isolated as a colourless solid (11 mg, 16%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.57 (d, $J_{H\text{-}P}$ = 13.2 Hz, 27H), 1.37 (dd, $J_{H\text{-}F}$ = 1.1 Hz, 1.1 Hz, 9H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ –118.5 to –118.7 (m), –151.9 to –152.1 (m); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 92.2 (p, J = 6.9 Hz).

Procedure for solution-phase aryl exchange experiments (Scheme S1)

A 1-dram vial was charged with (^{t}Bu$_3$P)AuAr^1,(0.1 mmol) , Ar^{2}H (4.0 equiv.), KO^{t}Bu (4.0 equiv.), and DMF (0.3 mL). The reaction mixture was stirred at 50 °C for 15 h, diluted with CH_2Cl_2 (5.0 mL) and filtered through a Celite plug. The filtrate was concentrated under reduced pressure, and product ratios were determined from ^{31}P NMR ($CDCl_3$) signal relative integrations.



Scheme S1. Solution-phase aryl exchange experiments.

Procedure for Scheme 7

The possible intermediacy of (^{t}Bu$_3$P)AuO^{t}Bu (**6**) in the formation of C–H aurated complexes was examined by a modified version of Procedure B1: (^{t}Bu$_3$P)AuCl (43 mg, 0.10 mmol) and KO^{t}Bu (13 mg, 0.12 mmol, 1.2 equiv.) were subjected to milling for 1 h at 30 Hz. Arene (4.0 equiv.) was subsequently added, and milling was continued for another 1 h. After workup, product yields were determined by ^{31}P NMR spectroscopy.

In a separate experiment, the reaction mixture resulting from milling (^{t}Bu$_3$P)AuCl (43 mg, 0.10 mmol) with KO^{t}Bu (22 mg, 0.20 mmol, 2.0 equiv.) was suspended in C_6D_6 and filtered through a Celite plug. The components of the filtrate solution were subsequently analysed by NMR spectroscopy, with the major observed signals consistent with those expected for **6** (Figure S3): **^{1}H NMR** (400 MHz, C_6D_6) δ 1.78 (s, 9H), 1.08 (d, J = 13.2 Hz, 27H); **^{13}C NMR** (101 MHz, C_6D_6) δ 71.7 (d, $J_{C\text{-}P}$ = 2 Hz), 38.0 (d, $J_{C\text{-}P}$ = 21 Hz), 36.9 (d, $J_{C\text{-}P}$ = 2 Hz), 31.5 (d, $J_{C\text{-}P}$ = 4 Hz); **^{31}P NMR** (162 MHz, C_6D_6) δ 81.43; **1D DOSY** (400 MHz, C_6D_6) D = 7.6 x 10^{-6} cm^2/sec (25 °C, array size = 15, diffusion delay = 100 ms, diffusion gradient length = 2 ms), estimated using MestreNova software to correspond to a molecular weight of 461 g/mol (cf. expected MW = 472 g/mol). **HRMS** (Nanospray) calcd. for $C_{16}H_{37}AuOP$ $[M+H]^+$: 473.2248, found 473.2251.

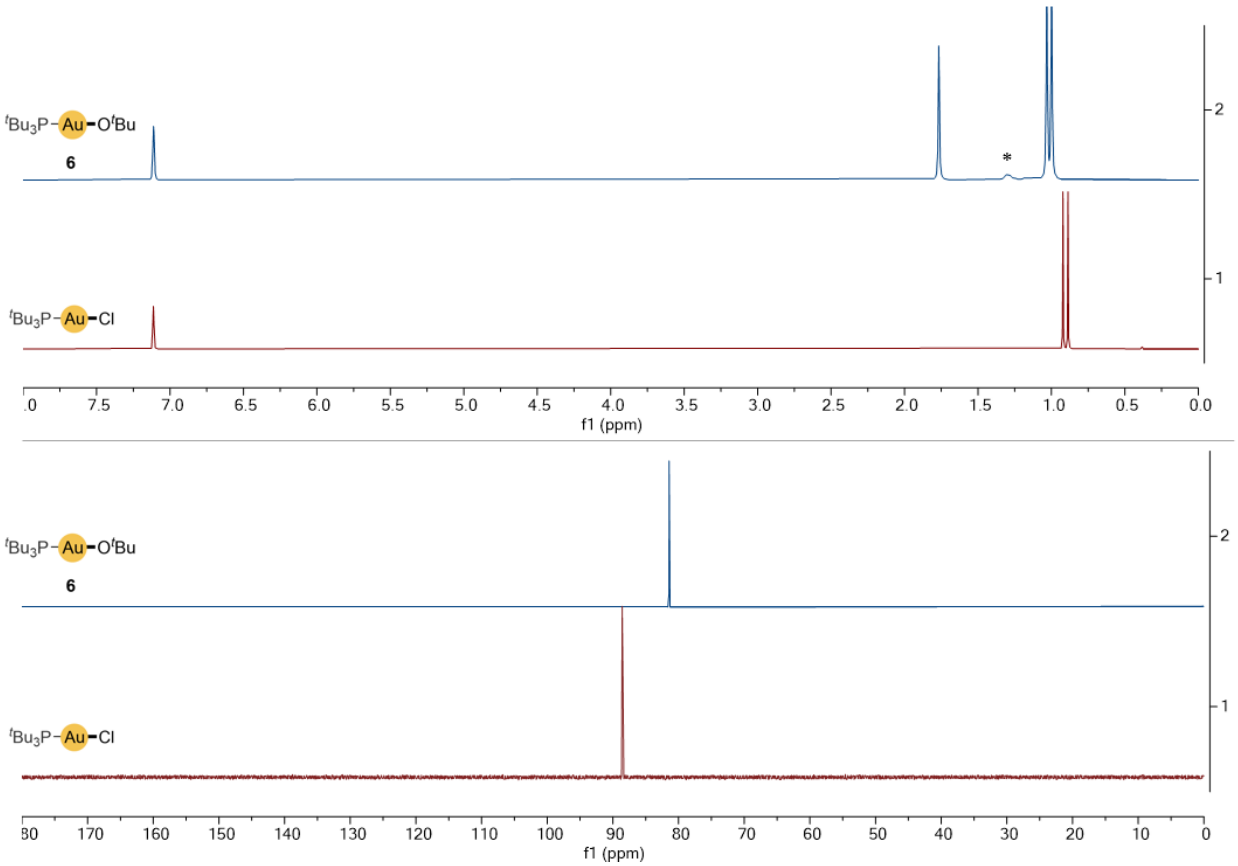


Figure S3: Comparison of the ^{1}H NMR (top) and ^{31}P NMR (bottom) spectra of **6** (blue) and (^{t}Bu$_3$P)AuCl (red). The peak in the ^{1}H spectrum marked by an asterisk (*) was assigned to residual KO^{t}Bu.

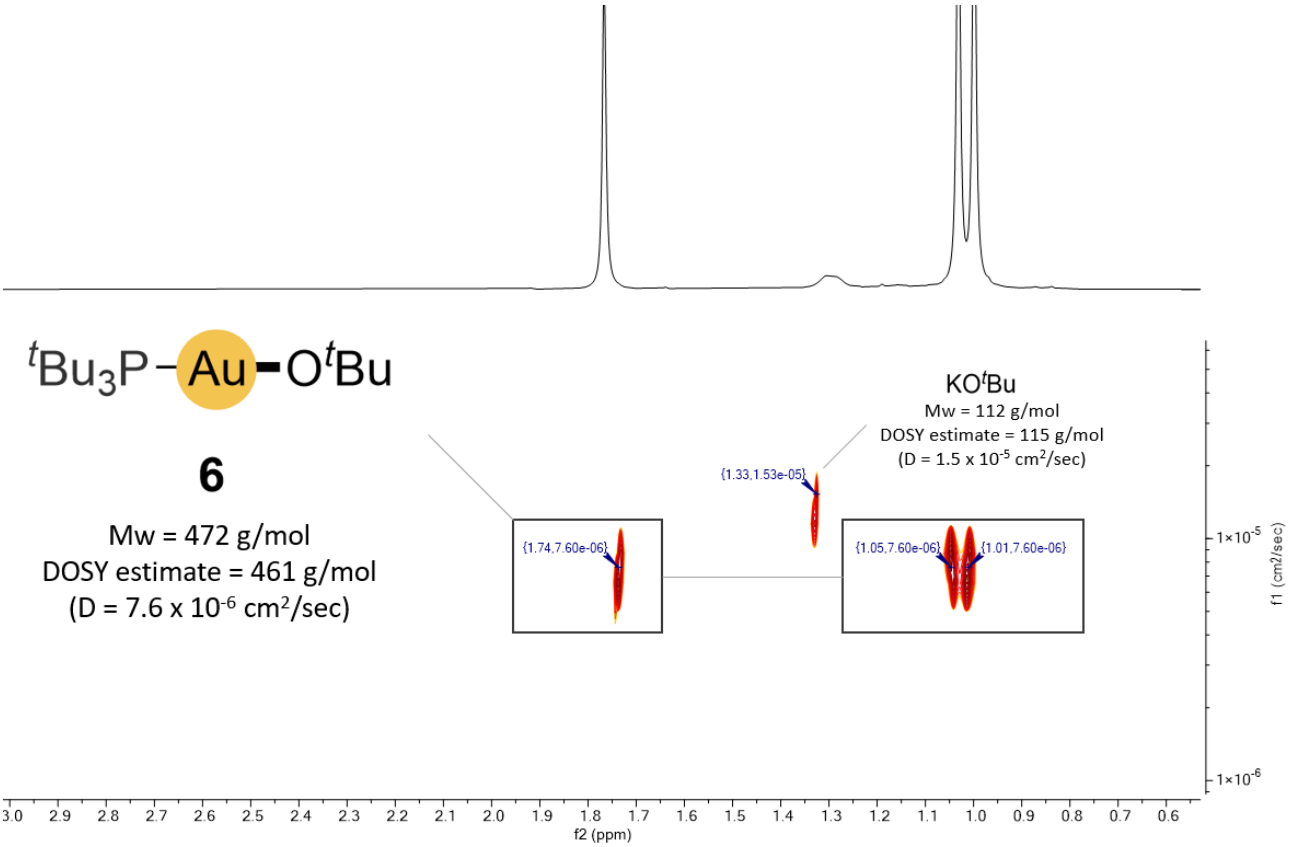
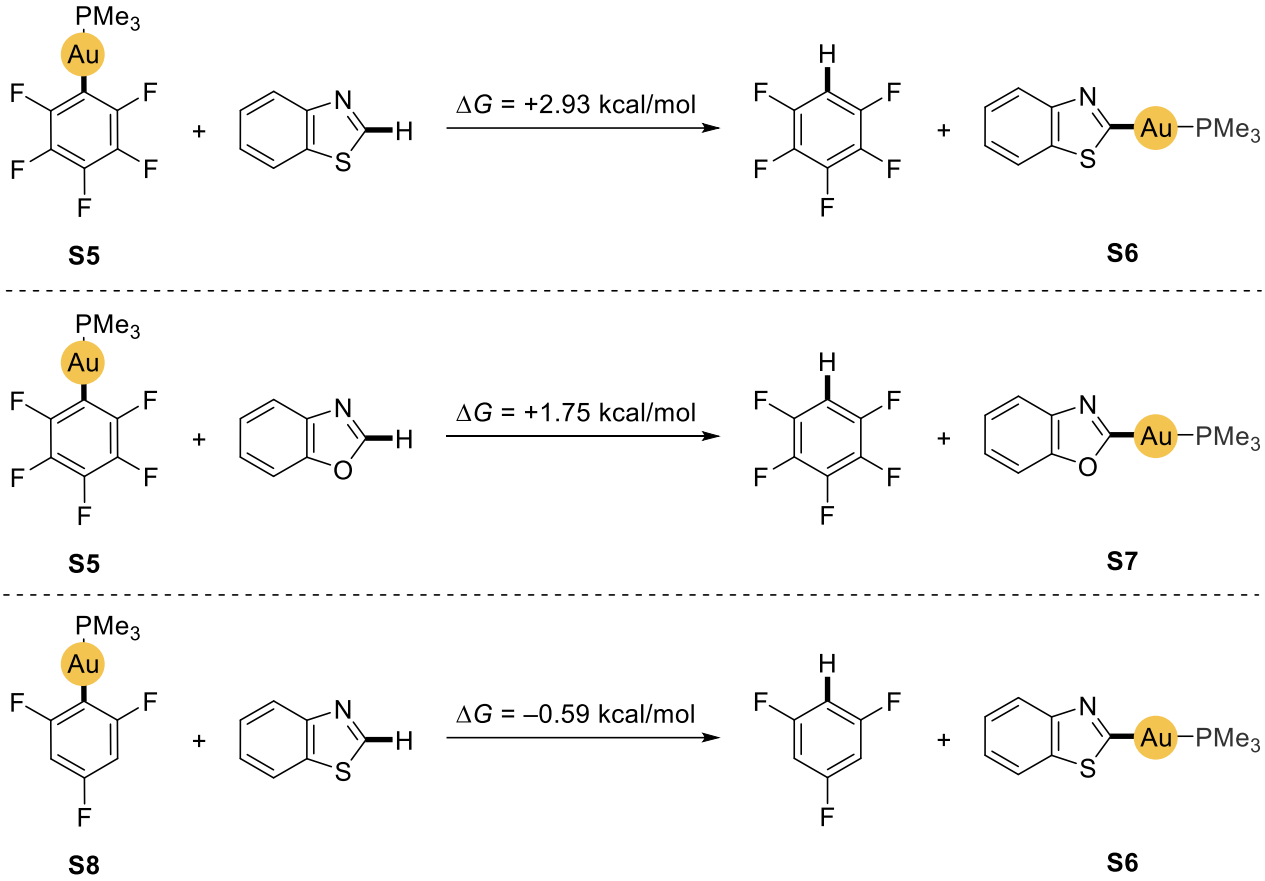


Figure S4: DOSY spectrum (C_6D_6) of reaction mixture from milling ($^tBu_3P$)AuCl with KO^{t}Bu.

Computational details

All calculations were performed using Gaussian09. Geometries were optimized at the DFT level of theory with the hybrid PBE0[17] exchange-correlation functional and the TZVP[18] basis set applied to all non-metal atoms and the SDD[19] basis set applied to Au. Solvent-phase (benzene) enthalpy and free energy values were calculated using the CPCM[20,21] solvation model. Geometry optimizations were performed using an ultrafine integration grid without imposed symmetry or other constraints. Vibrational frequencies were calculated to show that the optimized structures were minima on the potential energy surface.

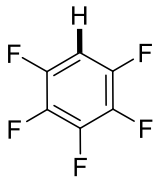


Scheme S2. Calculated (DFT) solvent-phase (benzene) free energy (Δ*G*, 298K) values for exchange between haloaryl and heteroaryl groups of $Me_3PAu(I)$ complexes.

Table S1. Total energies of calculated species

Molecule	PBE0/TZVP/SDD	
	ΔH_{298K} (Hartree)	ΔG_{298K} (Hartree)
pentafluorobenzene	–727.876320	–727.919975
S5	–1323.825866	–1323.894296
benzothiazole	–722.180483	–722.218725
S6	–1318.124365	–1318.188373
benzoxazole	–399.281864	–399.318691
S7	–995.227449	–995.290226
1,3,5-trifluorobenzene	–529.517694	–529.556910
S8	–1125.461400	–1125.525603

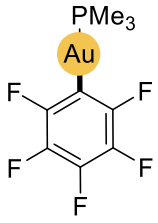
Optimized PBE0/TZVP/SDD Cartesian coordinates (Å)



pentafluorobenzene

0 1

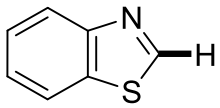
C	-1.18766	-0.96288	0.00000
C	-1.20269	0.42276	0.00000
C	0.00000	-1.66708	0.00000
C	0.00000	1.11273	0.00000
C	1.20269	0.42276	0.00000
C	1.18766	-0.96288	0.00000
F	-2.34866	-1.61224	0.00000
F	-2.34843	1.09143	0.00000
F	0.00000	2.43683	0.00000
F	2.34843	1.09143	0.00000
F	2.34866	-1.61224	0.00000
H	0.00000	-2.74931	0.00000



S5

0 1

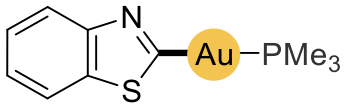
C	1.86532	-1.17050	0.00092
C	3.25067	-1.19569	-0.00058
C	1.12683	-0.00085	0.00167
C	3.94673	0.00129	-0.00140
C	3.24889	1.19725	-0.00059
C	1.86363	1.16990	0.00085
F	1.24370	-2.36319	0.00145
F	3.92304	-2.34759	-0.00137
F	5.27692	0.00228	-0.00290
F	3.91950	2.35018	-0.00135
F	1.24010	2.36160	0.00140
Au	-0.93561	-0.00131	0.00192
P	-3.25391	0.00055	-0.00152
C	-4.00300	1.64061	-0.30910
H	-3.66982	2.01497	-1.27777
H	-3.67464	2.33901	0.46155
H	-5.09308	1.57358	-0.29963
C	-4.01520	-0.55275	1.56706
H	-3.69018	-1.56998	1.78862
H	-5.10471	-0.52588	1.49522
H	-3.68792	0.09848	2.37833
C	-4.00658	-1.08188	-1.26951
H	-3.68003	-0.76105	-2.25939
H	-5.09647	-1.03902	-1.21366
H	-3.67440	-2.10878	-1.11285



benzothiazole

0 1

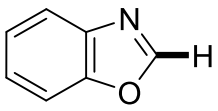
C	2.36714	-0.83833	0.00000
C	2.37636	0.56134	0.00000
C	1.19662	1.28364	0.00000
C	0.00000	0.57532	0.00000
C	-0.02405	-0.83245	0.00000
C	1.17824	-1.54052	0.00000
N	-1.28210	-1.40205	0.00000
C	-2.18730	-0.49130	0.00000
S	-1.63831	1.17190	0.00000
H	1.15661	-2.62395	0.00000
H	3.30818	-1.37620	0.00000
H	3.32287	1.08977	0.00000
H	1.20818	2.36711	0.00000
H	-3.25028	-0.69890	0.00000



S6

0 1

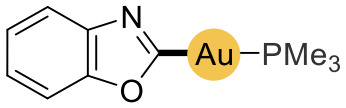
C	5.54928	1.17464	0.00114
C	5.82073	-0.19786	0.00101
C	4.79261	-1.12499	0.00040
C	3.48204	-0.65788	-0.00002
C	3.19562	0.72109	0.00010
C	4.24771	1.63907	0.00073
N	1.85573	1.05358	-0.00022
C	1.07854	0.01608	-0.00068
S	1.97792	-1.53121	-0.00066
H	4.02542	2.70010	0.00084
H	6.37202	1.88103	0.00161
H	6.84917	-0.54178	0.00137
H	5.00666	-2.18763	0.00034
Au	-0.96207	0.02756	-0.00077
P	-3.29087	0.07579	0.00117
C	-4.08193	-1.40177	-0.73293
C	-4.04132	0.20417	1.66502
H	-5.13138	0.22244	1.59916
H	-3.69083	1.11649	2.14918
H	-3.72794	-0.64805	2.26928
H	-5.16999	-1.31344	-0.69836
H	-3.77162	-2.29048	-0.18205
H	-3.75832	-1.50777	-1.76905
C	-4.01364	1.47615	-0.92815
H	-3.66718	2.41544	-0.49529
H	-5.10477	1.44021	-0.89609
H	-3.67907	1.43114	-1.96531



benzoxazole

0 1

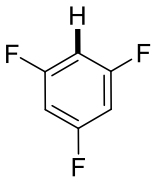
C	2.09560	0.69244	0.00000
C	2.08102	-0.70794	0.00000
C	0.89268	-1.42607	0.00000
C	-0.25935	-0.66703	0.00000
C	-0.27283	0.72633	0.00000
C	0.92389	1.43265	0.00000
N	-1.59757	1.15525	0.00000
C	-2.27349	0.06573	0.00000
O	-1.55871	-1.08843	0.00000
H	0.93212	2.51590	0.00000
H	3.04978	1.20668	0.00000
H	3.02209	-1.24566	0.00000
H	0.87111	-2.50861	0.00000
H	-3.34761	-0.04433	0.00000



S7

0 1

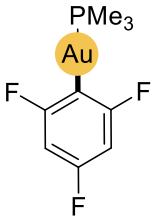
C	5.65057	0.62302	-0.00050
C	5.59659	-0.77541	-0.00012
C	4.38419	-1.45523	0.00027
C	3.24909	-0.66866	0.00029
C	3.27746	0.72413	-0.00001
C	4.49622	1.39308	-0.00044
N	1.97004	1.18962	0.00026
C	1.21396	0.13427	0.00050
O	1.94663	-1.05072	0.00059
H	4.53573	2.47620	-0.00070
H	6.61828	1.11236	-0.00084
H	6.52122	-1.34177	-0.00014
H	4.33314	-2.53741	0.00057
Au	-0.82032	0.03287	0.00001
P	-3.14590	-0.03601	0.00016
C	-3.86298	-1.43259	-0.93907
C	-3.89714	-0.17924	1.66228
H	-4.98696	-0.20216	1.59412
H	-3.58868	0.67080	2.27207
H	-3.54357	-1.09299	2.14140
H	-4.95415	-1.40151	-0.90394
H	-3.51197	-2.37364	-0.51396
H	-3.53140	-1.37804	-1.97667
C	-3.93934	1.44455	-0.72402
H	-3.61195	1.56091	-1.75782
H	-3.63332	2.32925	-0.16442
H	-5.02722	1.35256	-0.69441



1,3,5-fluorobenzene

0 1

C	-0.16107	1.35034	0.00000
C	-1.29029	0.55293	0.00000
C	1.12404	0.84097	0.00000
C	-1.08892	-0.81470	0.00000
C	0.16629	-1.39390	0.00000
C	1.25001	-0.53566	0.00000
F	-0.31943	2.67813	0.00000
H	-2.28447	0.97899	0.00000
F	-2.15969	-1.61566	0.00000
H	0.29454	-2.46789	0.00000
F	2.47906	-1.06246	0.00000
H	1.99007	1.48897	0.00000



S8

0 1

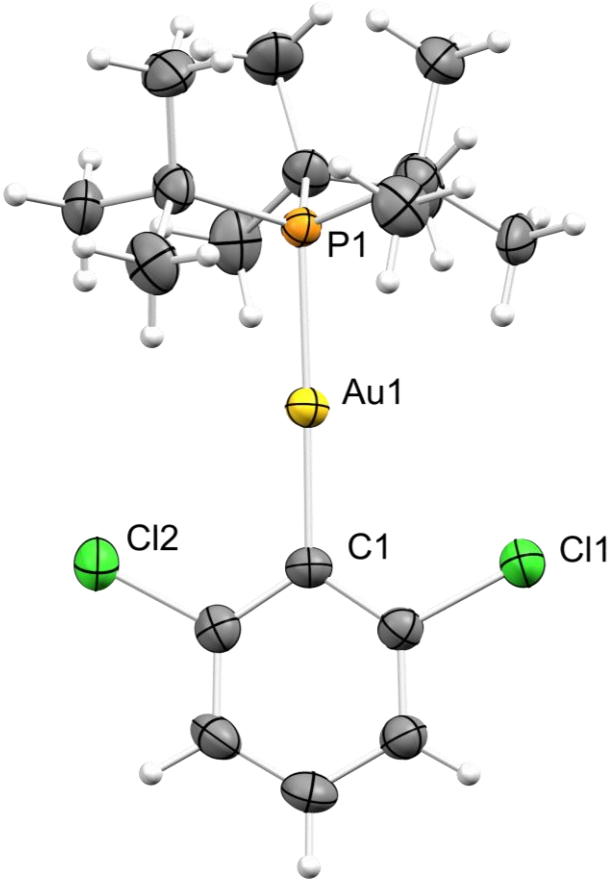
C	2.22118	-1.15891	0.00034
C	3.60562	-1.20888	-0.00076
C	1.45993	-0.00060	0.00096
C	4.26955	0.00122	-0.00137
C	3.60409	1.21051	-0.00073
C	2.21974	1.15870	0.00029
F	1.58298	-2.35069	0.00087
H	4.14129	-2.14911	-0.00131
F	5.61353	0.00208	-0.00251
H	4.13853	2.15136	-0.00112
F	1.57992	2.34963	0.00075
Au	-0.59764	-0.00103	0.00149
P	-2.91731	0.00047	-0.00103
C	-3.67219	1.63902	-0.30741
H	-3.34051	2.01463	-1.27613
H	-3.34425	2.33795	0.46297
H	-4.76221	1.57020	-0.29697
C	-3.68278	-0.55298	1.56648
H	-3.35786	-1.57018	1.78851
H	-4.77230	-0.52626	1.49388
H	-3.35601	0.09779	2.37837
C	-3.67551	-1.08071	-1.26802
H	-3.34965	-0.76019	-2.25827
H	-4.76535	-1.03703	-1.21092
H	-3.34387	-2.10799	-1.11244

Crystallographic data

Table 1. Crystal data and structure refinement for 3d.

CCDC No.	2007939
Empirical formula	$C_{18}H_{30}AuCl_2P$
Formula weight	545.25
Temperature/K	170
Crystal system	triclinic
Space group	P-1
a/Å	8.63460(10)
b/Å	11.49630(10)
c/Å	11.8740(2)
α/°	65.9950(10)
β/°	87.9480(10)
γ/°	71.8100(10)
Volume/Å^3	1017.27(2)
Z	2
ρ_{calc}g/cm^3	1.780
μ/mm^{-1}	7.568
F(000)	532.0
Crystal size/mm^3	0.1 × 0.06 × 0.03
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.102 to 69.31
Index ranges	$-13 \leq h \leq 13$, $-18 \leq k \leq 18$, $-18 \leq l \leq 18$
Reflections collected	14472
Independent reflections	14472 [R_{int} = ?, R_{sigma} = 0.0100]
Data/restraints/parameters	14472/0/209
Goodness-of-fit on F^2	1.127
Final R indexes [I>=2σ (I)]	R_1 = 0.0538, wR_2 = 0.1384
Final R indexes [all data]	R_1 = 0.0552, wR_2 = 0.1395
Largest diff. peak/hole / e Å^{-3}	2.54/-2.47

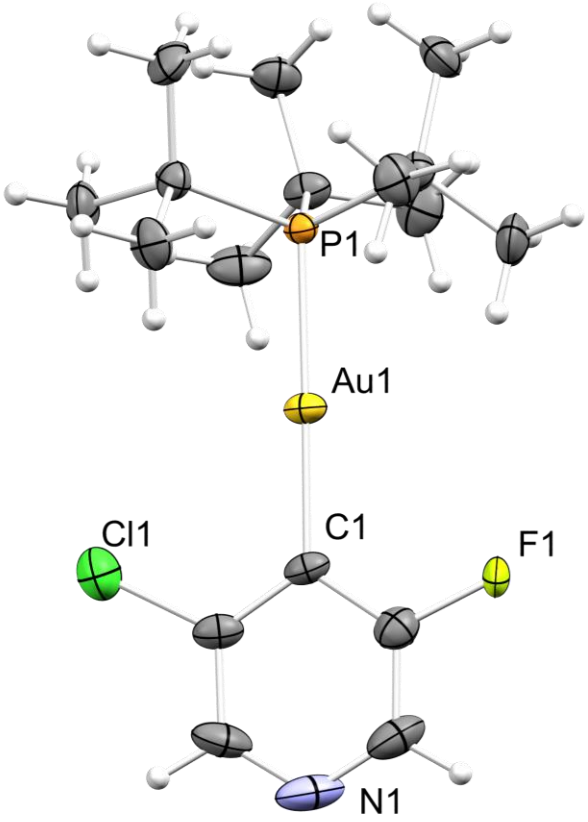
NOTE: The data collected for this crystal were integrated as a twin (0 0 1 reciprocal lattice) with two components 0.7458(7) : 0.2542(7) using CrysAlisPro 1.171.39.46 (Rigaku OD, 2018).



ORTEP plot (50% probability ellipsoids) of **3d**. Selected bond lengths [Å] and angles [°]: Au1-P1 2.2948(15), Au1-C1 2.039(6), C1-Au1-P1 178.73(19).

Table 2. Crystal data and structure refinement for 3f.

CCDC No.	2007940
Empirical formula	$C_{17}H_{29}AuClFNP$
Formula weight	529.80
Temperature/K	170
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	8.6986(10)
b/Å	18.586(2)
c/Å	12.1084(13)
α/°	90
β/°	90.975(2)
γ/°	90
Volume/Å^3	1957.3(4)
Z	4
ρ_{calc}g/cm^3	1.798
μ/mm^{-1}	7.740
F(000)	1032.0
Crystal size/mm^3	0.12 × 0.1 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.016 to 61.41
Index ranges	$-12 \leq h \leq 11$, $-26 \leq k \leq 26$, $-17 \leq l \leq 17$
Reflections collected	28991
Independent reflections	6049 [R_{int} = 0.0621, R_{sigma} = 0.0583]
Data/restraints/parameters	6049/3/208
Goodness-of-fit on F^2	1.067
Final R indexes [I>=2σ (I)]	R_1 = 0.0322, wR_2 = 0.0719
Final R indexes [all data]	R_1 = 0.0441, wR_2 = 0.0745
Largest diff. peak/hole / e Å^{-3}	1.60/-1.60



ORTEP plot (50% probability ellipsoids) of **3f**. Selected bond lengths [Å] and angles [°]:Au1-P1 2.3007(10), Au1-C1 2.045(4), C1-Au1-P1 178.49(12).

References

1 F. J. L. L. Ingner, A. C. Schmitt, A. Orthaber, P. J. Gates and L. T. Pilarski, *ChemSusChem*, 2020, **13**, 2032–2037.

2 Bruker, *SAINT*, Bruker AXS Inc.:, Madison, Wisconsin, USA, 2007.

3 Bruker, *SADABS*, Bruker AXS Inc.:, Madison, Wisconsin, USA, 2001.

4 G. M. Sheldrick and IUCr, *Acta Crystallogr. Sect. A Found. Crystallogr.*, 2008, **64**, 112–122.

5 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339–341.

6 N. A. Barnes, K. R. Flower, S. A. Fyyaz, S. M. Godfrey, A. T. McGown, P. J. Miles, R. G. Pritchard and J. E. Warren, *CrystEngComm*, 2010, **12**, 784–794.

7 D. V. Partyka, M. Zeller, A. D. Hunter and T. G. Gray, *Angew. Chemie - Int. Ed.*, 2006, **45**, 8188–8191.

8 C. Croix, A. Balland-Longeau, H. Allouchi, M. Giorgi, A. Duchêne and J. Thibonnet, *J. Organomet. Chem.*, 2005, **690**, 4835–4843.

9 M. Peña-López, L. A. Sarandeses and J. Pérez Sestelo, *European J. Org. Chem.*, 2013, **2013**, 2545–2554.

10 C. Croix, C.-E. Sauvage, A. Balland-Longeau, A. Duchêne and J. Thibonnet, *J. Inorg. Organomet. Polym. Mater.*, 2008, **18**, 334–343.

11 M. Peña-López, M. Ayán-Varela, L. A. Sarandeses and J. P. Sestelo, *Org. Biomol. Chem.*, 2012, **10**, 1686–1694.

12 N. Ahlsten, G. J. P. P. Perry, X. C. Cambeiro, T. C. Boorman and I. Larrosa, *Catal. Sci. Technol.*, 2013, **3**, 2892.

13 P. Lu, T. C. Boorman, A. M. Z. Slawin and I. Larrosa, *J. Am. Chem. Soc.*, 2010, **132**, 5580–5581.

14 S. S. S. Dupuy, L. Crawford, M. Bühl, A. M. Z. Slawin and S. P. Nolan, *Adv. Synth. Catal.*, 2012, **354**, 2380–2386.

15 D. Partyka, A. Esswein, M. Zeller, A. Hunter, T. Gray, D. Partyka, A. Esswein, M. Zeller, A. Hunter and T. Gray, *Organometallics*, 2007, **26**, 3279–3282.

16 G. A. Artamkina, P. K. Sazonov, V. A. Ivushkin and I. P. Beletskaya, *Chem. – A Eur. J.*, 1998, **4**, 1169–1178.

17 C. Adamo and V. Barone, *J. Chem. Phys.*, 1999, **110**, 6158–6170.

18 N. Godbout, D. R. Salahub, J. Andzelm and E. Wimmer, *Can. J. Chem.*, 1992, **70**, 560–571.

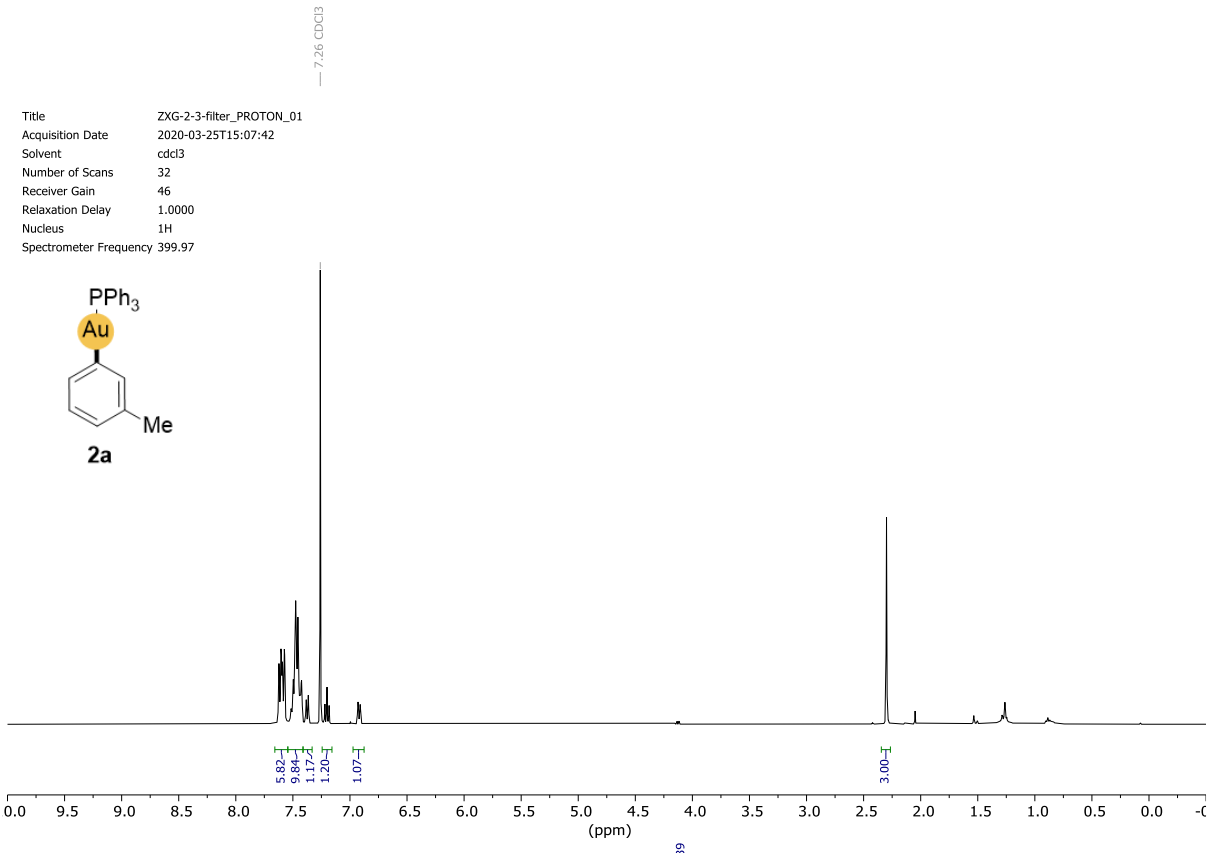
19 M. Dolg, U. Wedig, H. Stoll and H. Preuss, *J. Chem. Phys.*, 1987, **86**, 866–872.

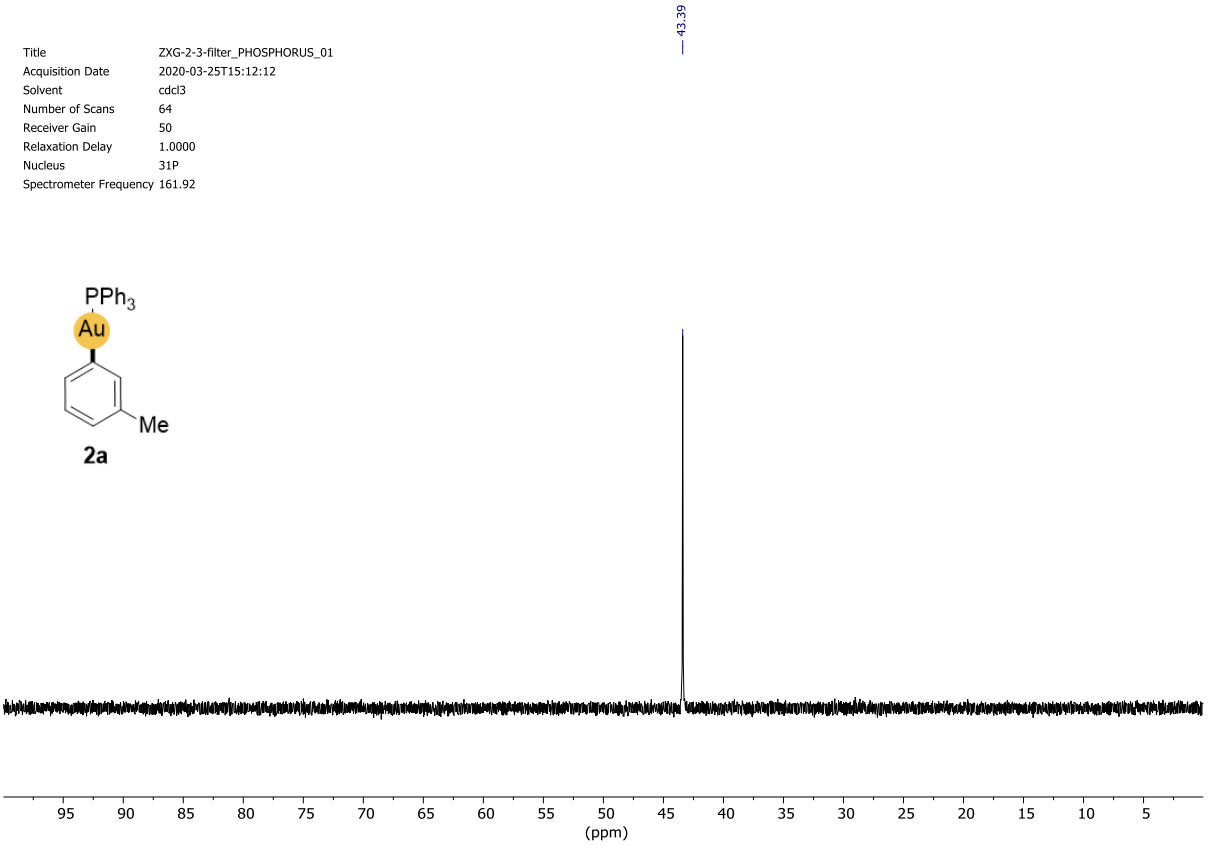
20 E. Cancès, B. Mennucci and J. Tomasi, *J. Chem. Phys.*, 1997, **107**, 3032–3041.

21 V. Barone, M. Cossi and J. Tomasi, *J. Chem. Phys.*, 1997, **107**, 3210–3221.

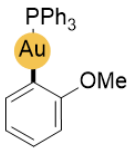
NMR Spectra

Transmetalation from boronic acids (Scheme 1)


7.26 CDCl3
Title ZXG-2-3-filter_PROTON_01
Acquisition Date 2020-03-25T15:07:42
Solvent cdcl3
Number of Scans 32
Receiver Gain 46
Relaxation Delay 1.0000
Nucleus 1H
Spectrometer Frequency 399.97
PPh3
Au
Me
2a
5.82
9.84
1.17
1.20
1.07
3.00
(ppm)

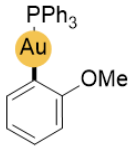

43.39
Title ZXG-2-3-filter_PHOSPHORUS_01
Acquisition Date 2020-03-25T15:12:12
Solvent cdcl3
Number of Scans 64
Receiver Gain 50
Relaxation Delay 1.0000
Nucleus 31P
Spectrometer Frequency 161.92
PPh3
Au
Me
2a
(ppm)

Title	ZXG-7-9-filter_PROTON_01
Acquisition Date	2020-03-27T16:54:10
Solvent	cdcl3
Number of Scans	32
Receiver Gain	46
Relaxation Delay	1.0000
Nucleus	1H
Spectrometer Frequency	399.97

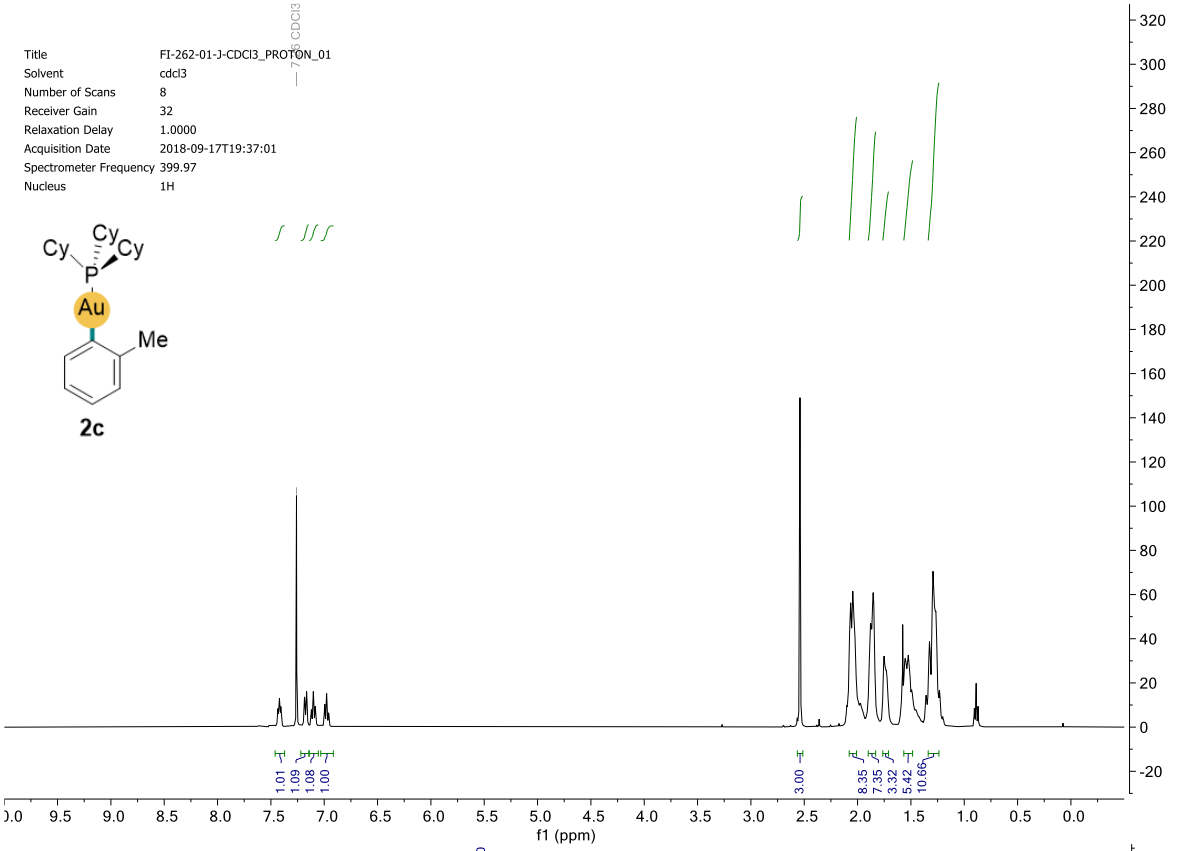


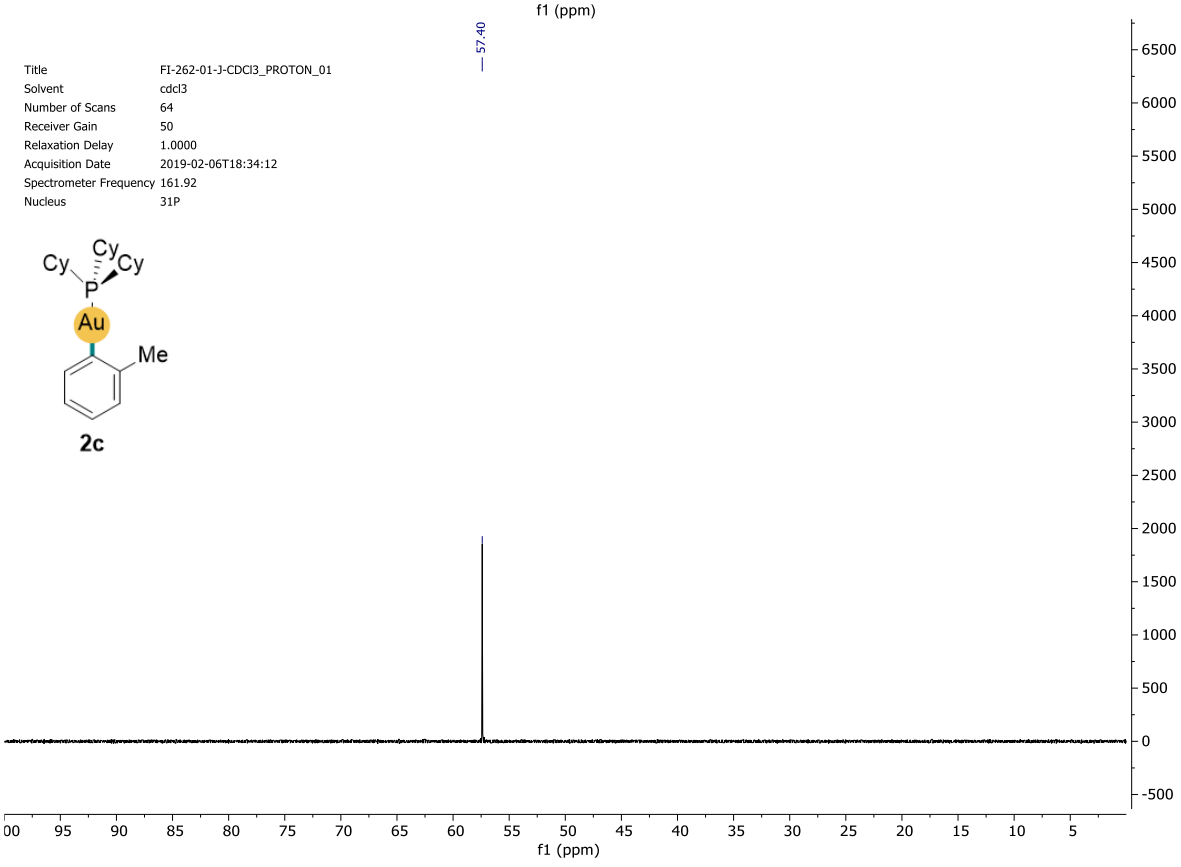
2b

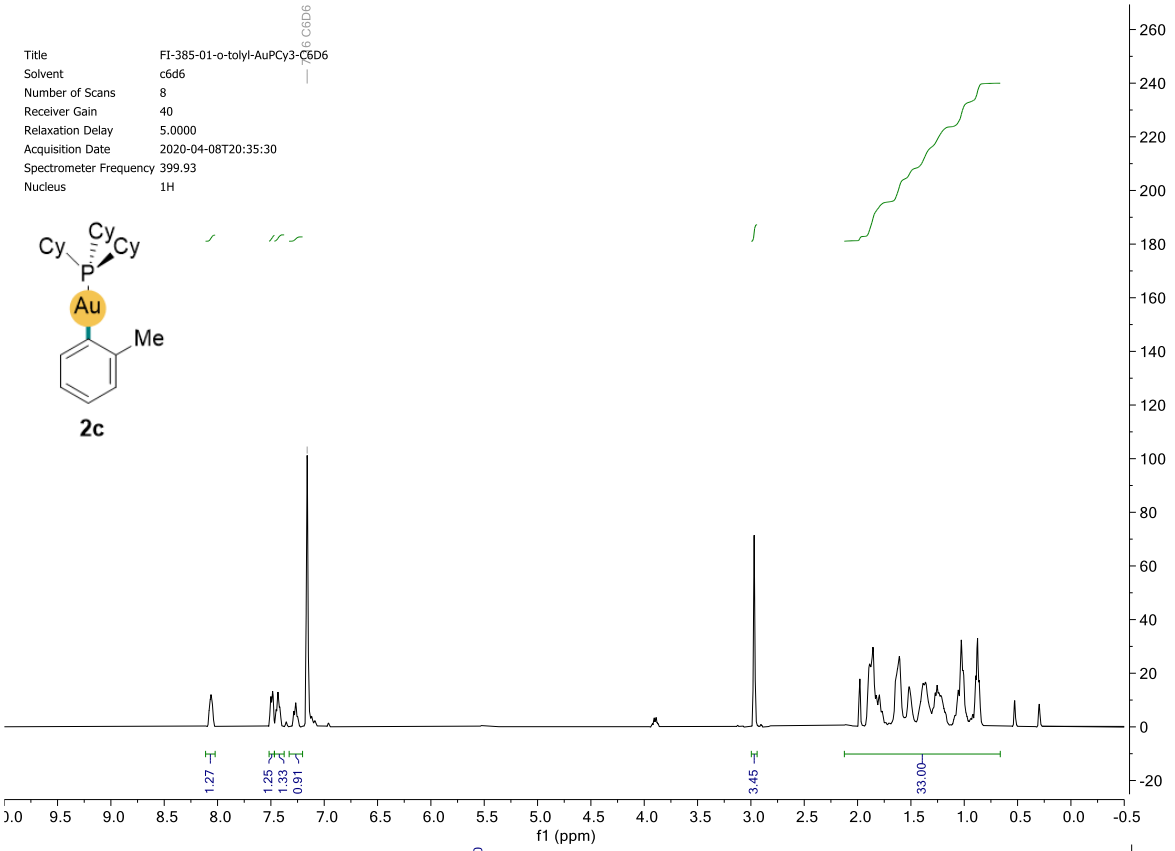
Title	ZXG-7-9-filter_PHOSPHORUS_01
Acquisition Date	2020-03-27T16:58:17
Solvent	cdcl3
Number of Scans	64
Receiver Gain	50
Relaxation Delay	1.0000
Nucleus	31P
Spectrometer Frequency	161.92

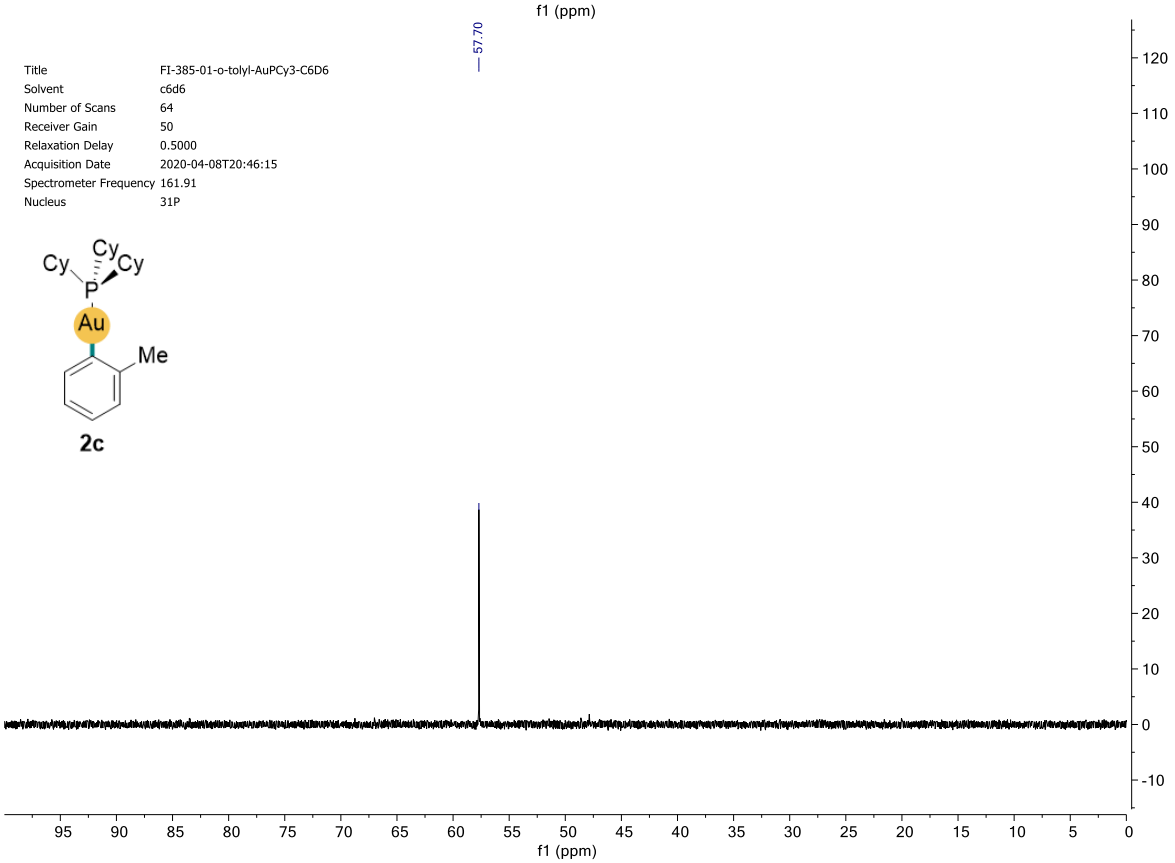


2b

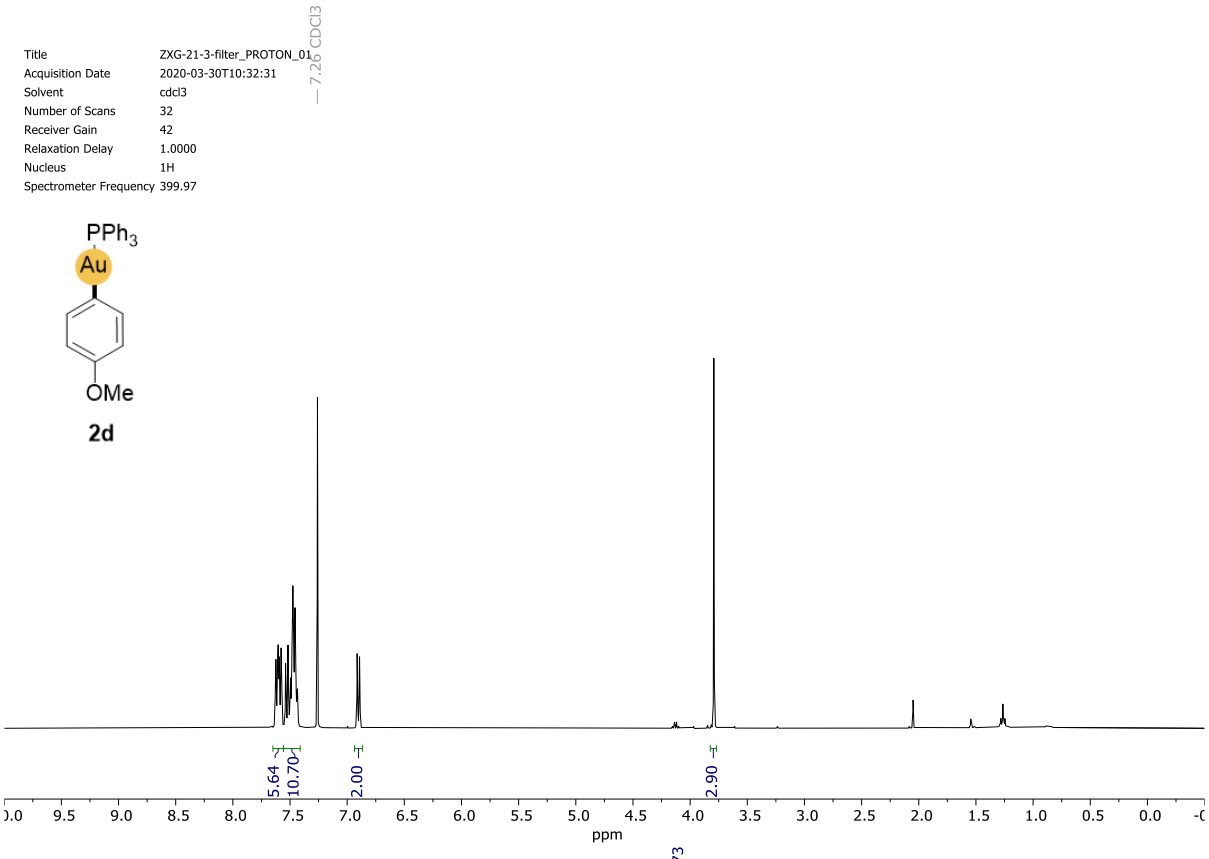

Title FI-262-01-J-CDCl3_PROTON_01
Solvent cdcl3
Number of Scans 8
Receiver Gain 32
Relaxation Delay 1.0000
Acquisition Date 2018-09-17T19:37:01
Spectrometer Frequency 399.97
Nucleus 1H
7.26 CDCl3
Cy
Cy
Cy
P
Au
Me
2c
1.01
1.09
1.08
1.00
3.00
8.35
7.35
3.32
5.42
10.66
f1 (ppm)


57.40
Title FI-262-01-J-CDCl3_PROTON_01
Solvent cdcl3
Number of Scans 64
Receiver Gain 50
Relaxation Delay 1.0000
Acquisition Date 2019-02-06T18:34:12
Spectrometer Frequency 161.92
Nucleus 31P
Cy
Cy
Cy
P
Au
Me
2c
f1 (ppm)

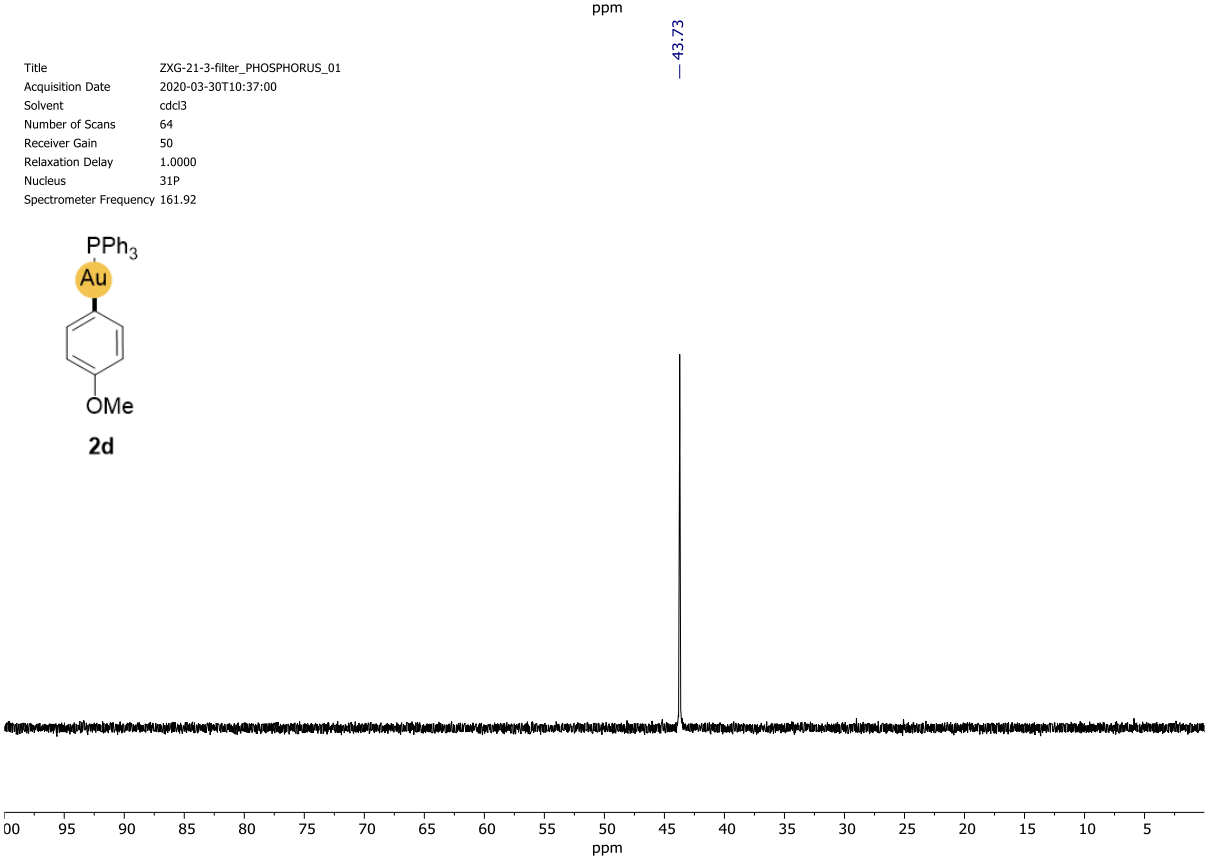

Title FI-385-01-o-tolyl-AuPCy3-C6D6
Solvent c6d6
Number of Scans 8
Receiver Gain 40
Relaxation Delay 5.0000
Acquisition Date 2020-04-08T20:35:30
Spectrometer Frequency 399.93
Nucleus 1H
Cy
Cy
Cy
P
Au
Me
2c
1.27
1.25
1.33
0.91
3.45
33.00
f1 (ppm)


57.70
Title FI-385-01-o-tolyl-AuPCy3-C6D6
Solvent c6d6
Number of Scans 64
Receiver Gain 50
Relaxation Delay 0.5000
Acquisition Date 2020-04-08T20:46:15
Spectrometer Frequency 161.91
Nucleus 31P
Cy
Cy
Cy
P
Au
Me
2c
f1 (ppm)

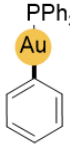
Title	ZXG-21-3-filter_PROTON_01
Acquisition Date	2020-03-30T10:32:31
Solvent	cdcl3
Number of Scans	32
Receiver Gain	42
Relaxation Delay	1.0000
Nucleus	1H
Spectrometer Frequency	399.97



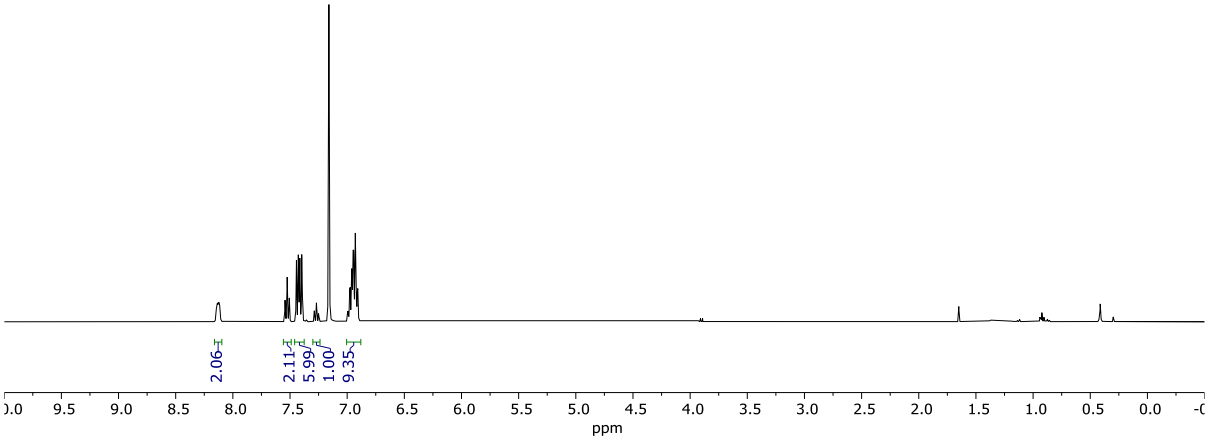
Title	ZXG-21-3-filter_PHOSPHORUS_01
Acquisition Date	2020-03-30T10:37:00
Solvent	cdcl3
Number of Scans	64
Receiver Gain	50
Relaxation Delay	1.0000
Nucleus	31P
Spectrometer Frequency	161.92



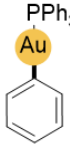
Title	ZXG-17-5-filter-SI_PROTON_01
Acquisition Date	2020-04-10T04:49:54
Solvent	c6d6
Number of Scans	32
Receiver Gain	42
Relaxation Delay	1.0000
Nucleus	1H
Spectrometer Frequency	399.97



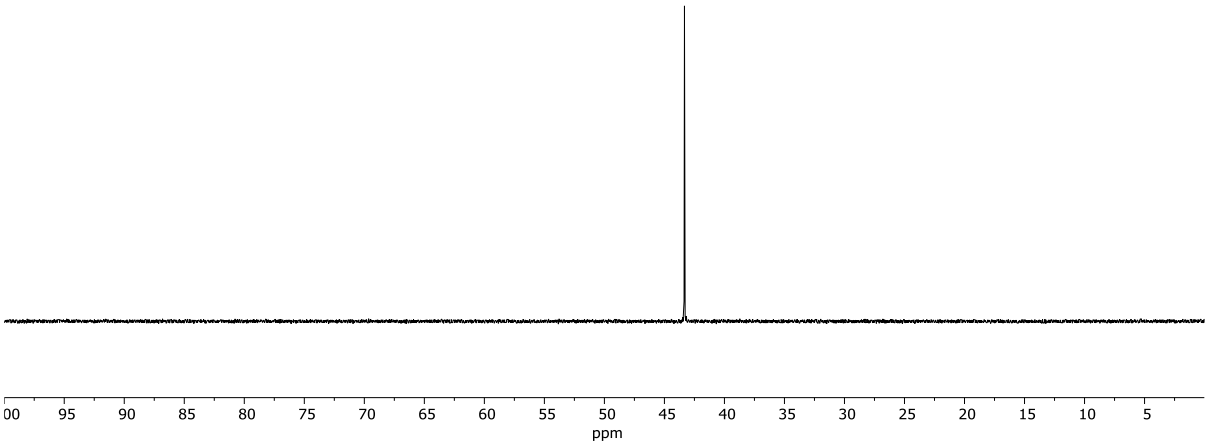
2e



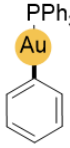
Title	ZXG-17-5-filter-SI_PHOSPHORUS_01
Acquisition Date	2020-04-10T04:54:21
Solvent	c6d6
Number of Scans	64
Receiver Gain	50
Relaxation Delay	1.0000
Nucleus	31P
Spectrometer Frequency	161.92



2e

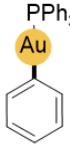


Title	ZXG-17-5-filter_PROTON_01
Acquisition Date	2020-04-09T09:11:13
Solvent	cdcl3
Number of Scans	32
Receiver Gain	46
Relaxation Delay	1.0000
Nucleus	1H
Spectrometer Frequency	399.97



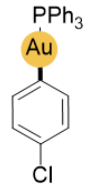
2e

Title	ZXG-17-5-filter_PHOSPHORUS_01
Acquisition Date	2020-04-09T09:15:49
Solvent	cdcl3
Number of Scans	64
Receiver Gain	50
Relaxation Delay	1.0000
Nucleus	31P
Spectrometer Frequency	161.92



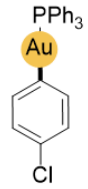
2e

Title	ZXG-25-1-filter3_PROTON_01
Acquisition Date	2020-04-06T10:39:17
Solvent	cdcl3
Number of Scans	32
Receiver Gain	44
Relaxation Delay	1.0000
Nucleus	1H
Spectrometer Frequency	399.97

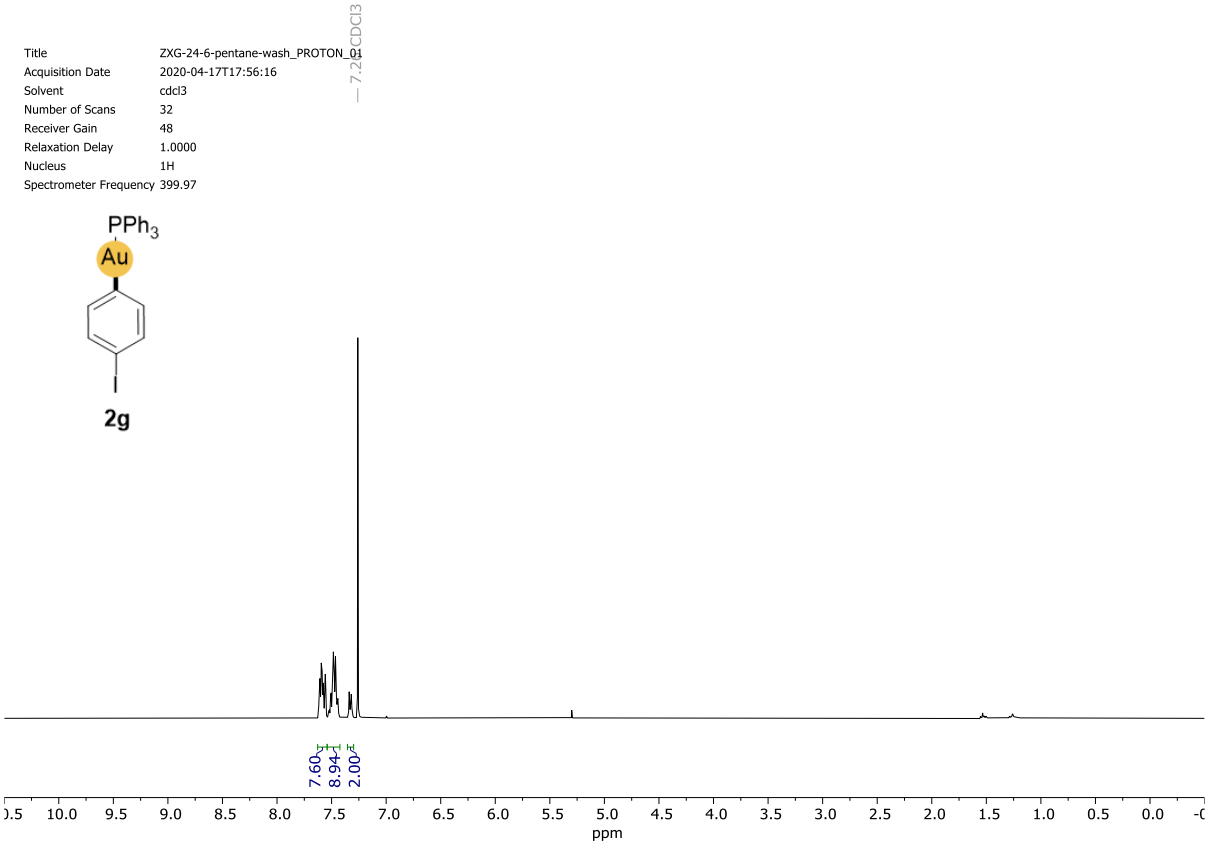


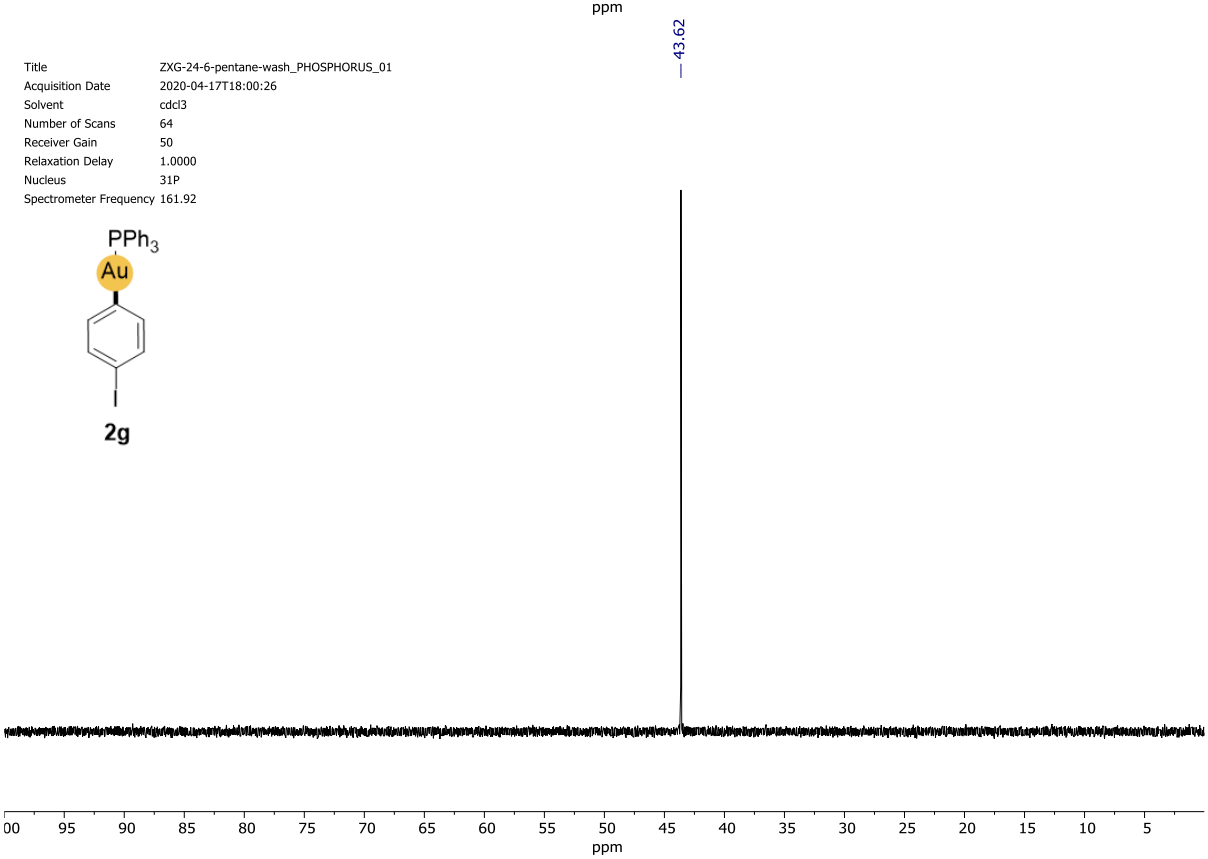
2f

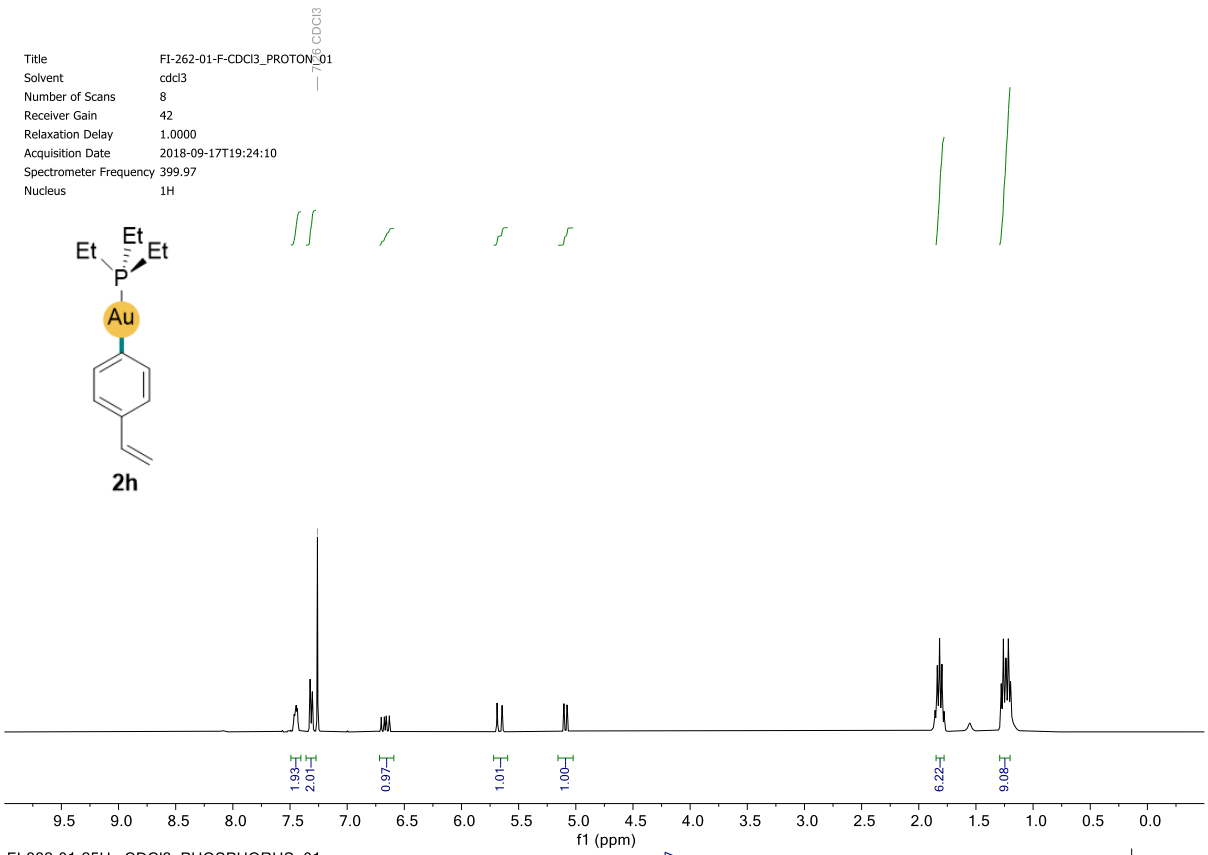
Title	ZXG-25-1-filter3_PHOSPHORUS_01
Acquisition Date	2020-04-06T10:43:51
Solvent	cdcl3
Number of Scans	64
Receiver Gain	50
Relaxation Delay	1.0000
Nucleus	31P
Spectrometer Frequency	161.92

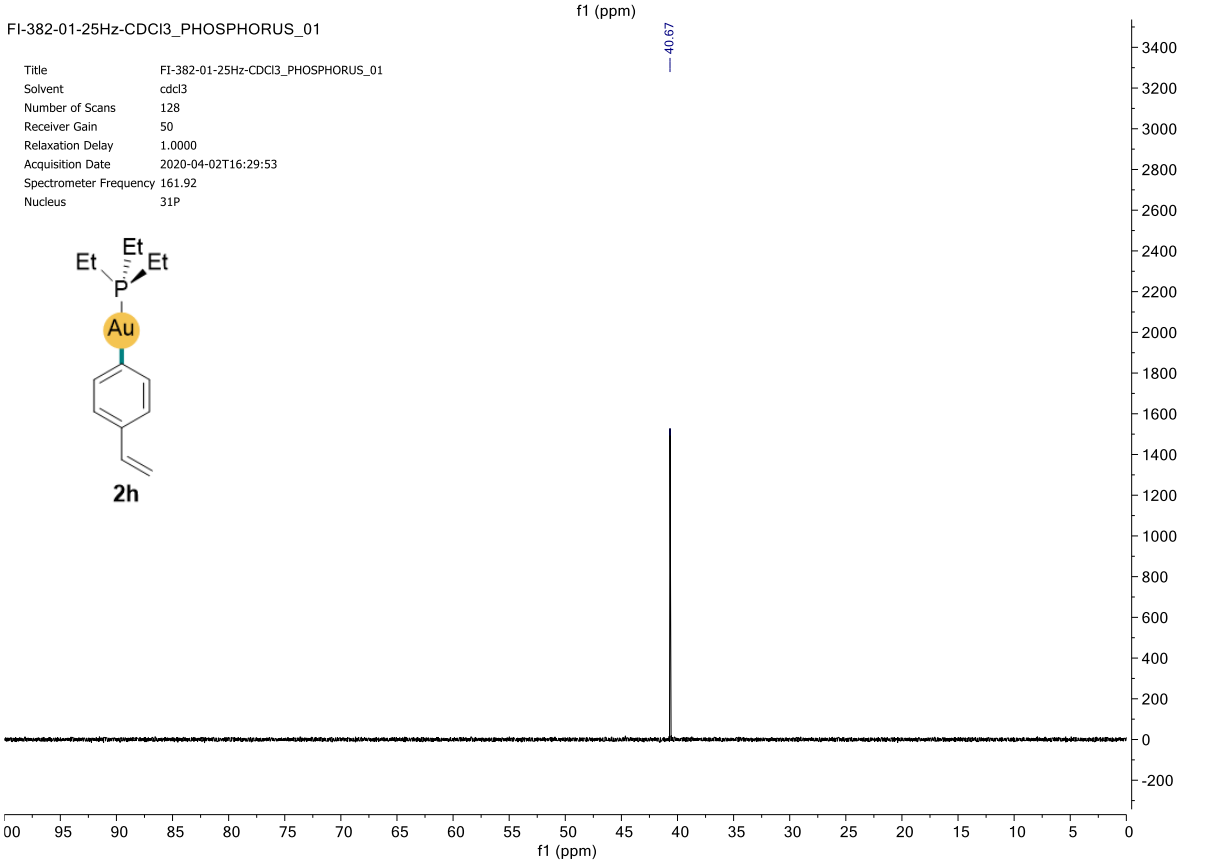


2f

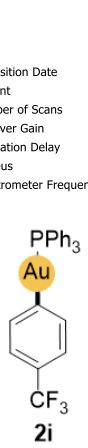

Title ZXG-24-6-pentane-wash_PROTON_01
Acquisition Date 2020-04-17T17:56:16
Solvent cdcl3
Number of Scans 32
Receiver Gain 48
Relaxation Delay 1.0000
Nucleus 1H
Spectrometer Frequency 399.97
7.26 CDCl3
PPh3
Au
2g
7.60
8.94
2.00
ppm


Title ZXG-24-6-pentane-wash_PHOSPHORUS_01
Acquisition Date 2020-04-17T18:00:26
Solvent cdcl3
Number of Scans 64
Receiver Gain 50
Relaxation Delay 1.0000
Nucleus 31P
Spectrometer Frequency 161.92
43.62
PPh3
Au
2g
ppm


Title FI-262-01-F-CDCl3_PROTON_01
Solvent cdcl3
Number of Scans 8
Receiver Gain 42
Relaxation Delay 1.0000
Acquisition Date 2018-09-17T19:24:10
Spectrometer Frequency 399.97
Nucleus 1H
7.26 CDCl3
Et
Et
Et
P
Au
2h
1.93
2.01
0.97
1.01
1.00
6.22
9.08
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

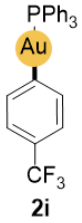

FI-382-01-25Hz-CDCl3_PHOSPHORUS_01
Title FI-382-01-25Hz-CDCl3_PHOSPHORUS_01
Solvent cdcl3
Number of Scans 128
Receiver Gain 50
Relaxation Delay 1.0000
Acquisition Date 2020-04-02T16:29:53
Spectrometer Frequency 161.92
Nucleus 31P
40.67
Et
Et
Et
P
Au
2h
3400 3200 3000 2800 2600 2400 2200 2000 1800 1600 1400 1200 1000 800 600 400 200 0 -200
00 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)

Title	ZXG-20-4-filter-SI-2_PROTON_01
Acquisition Date	2020-04-02T03:33:58
Solvent	c6d6
Number of Scans	32
Receiver Gain	42
Relaxation Delay	1.0000
Nucleus	1H
Spectrometer Frequency	399.97



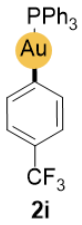
2i

Title	ZXG-20-4-filter_FLUORINE_01
Acquisition Date	2020-03-31T18:15:49
Solvent	c6d6
Number of Scans	64
Receiver Gain	60
Relaxation Delay	1.0000
Nucleus	19F
Spectrometer Frequency	376.31



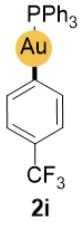
2i

Title	ZXG-20-4-filter_PHOSPHORUS_01
Acquisition Date	2020-03-31T18:20:23
Solvent	c6d6
Number of Scans	64
Receiver Gain	50
Relaxation Delay	1.0000
Nucleus	31P
Spectrometer Frequency	161.92



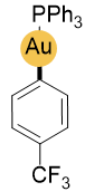
2i

Title	ZXG-20-4-filter2_PROTON_01
Acquisition Date	2020-04-03T11:37:07
Solvent	cdcl3
Number of Scans	32
Receiver Gain	48
Relaxation Delay	1.0000
Nucleus	1H
Spectrometer Frequency	399.97



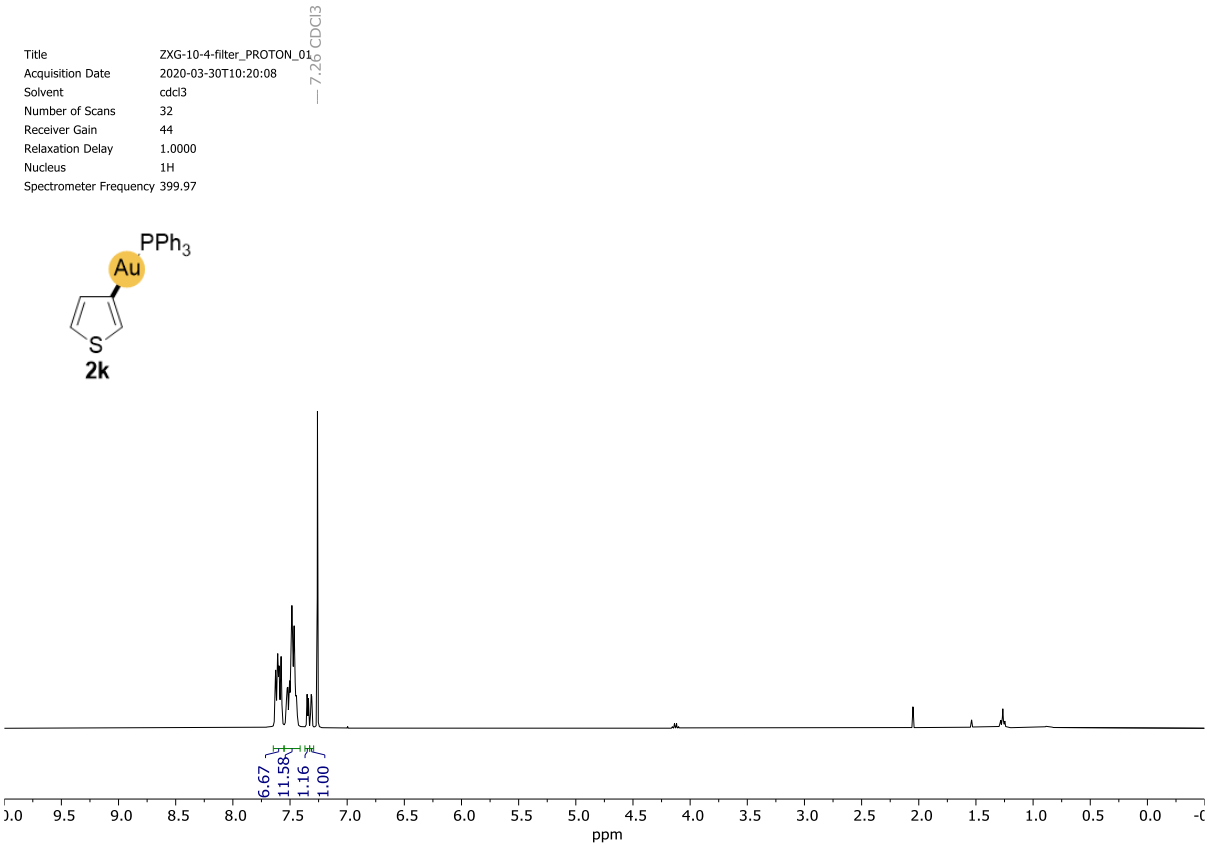
2i

Title	ZXG-20-4-filter-CDCl3_PHOSPHORUS_01
Acquisition Date	2020-04-01T16:55:59
Solvent	cdcl3
Number of Scans	64
Receiver Gain	50
Relaxation Delay	1.0000
Nucleus	31P
Spectrometer Frequency	161.92

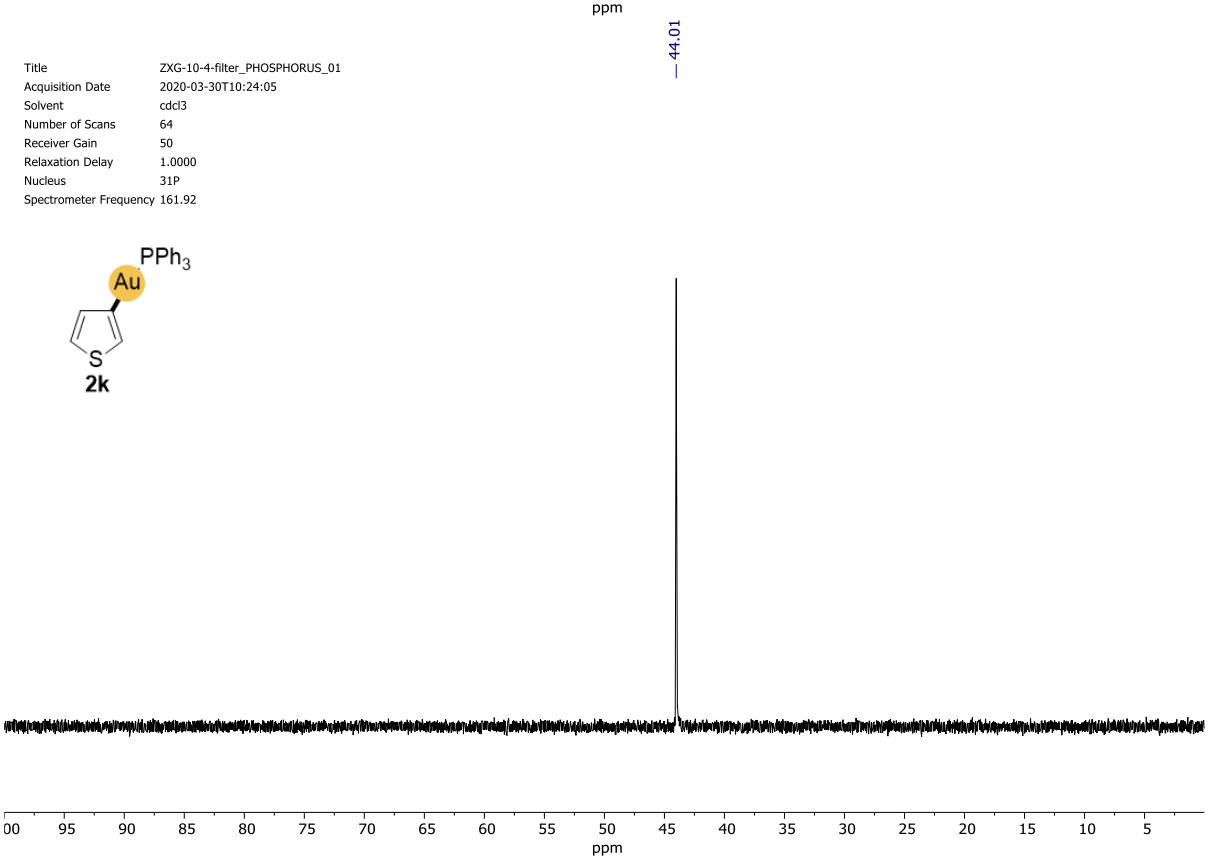


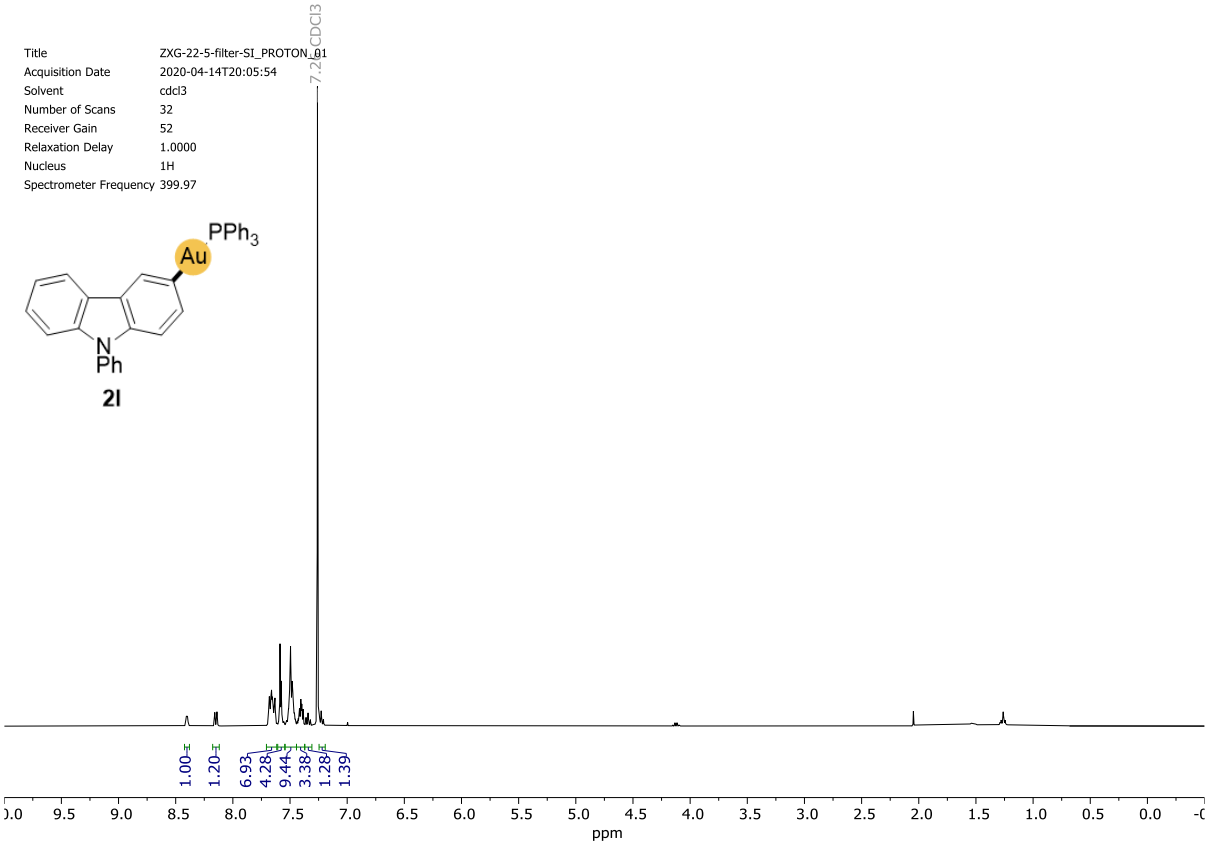
2i

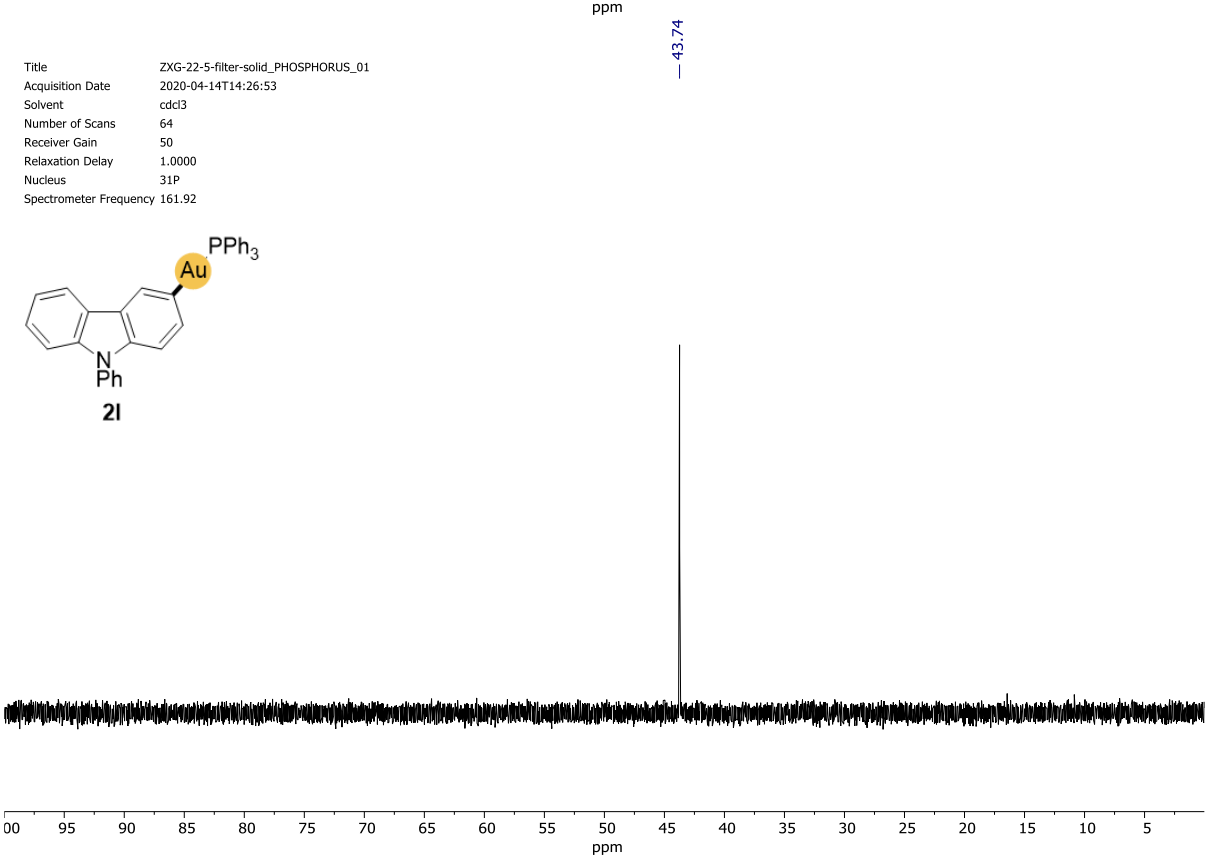
Title	ZXG-10-4-filter_PROTON_01
Acquisition Date	2020-03-30T10:20:08
Solvent	cdcl3
Number of Scans	32
Receiver Gain	44
Relaxation Delay	1.0000
Nucleus	1H
Spectrometer Frequency	399.97



Title	ZXG-10-4-filter_PHOSPHORUS_01
Acquisition Date	2020-03-30T10:24:05
Solvent	cdcl3
Number of Scans	64
Receiver Gain	50
Relaxation Delay	1.0000
Nucleus	31P
Spectrometer Frequency	161.92

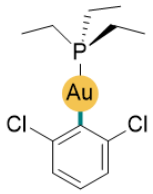



Title ZXG-22-5-filter-SI_PROTON_01
Acquisition Date 2020-04-14T20:05:54
Solvent cdcl3
Number of Scans 32
Receiver Gain 52
Relaxation Delay 1.0000
Nucleus 1H
Spectrometer Frequency 399.97
7.26 CDCl3
PPh3
Au
N
Ph
2l
1.00
1.20
6.93
4.28
9.44
3.38
1.28
1.39
ppm


Title ZXG-22-5-filter-solid_PHOSPHORUS_01
Acquisition Date 2020-04-14T14:26:53
Solvent cdcl3
Number of Scans 64
Receiver Gain 50
Relaxation Delay 1.0000
Nucleus 31P
Spectrometer Frequency 161.92
43.74
PPh3
Au
N
Ph
2l
ppm

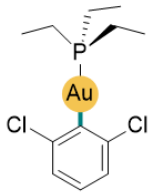
C-H Auration of haloarenes (Scheme 2)

Title	FI-261-07-SiO2Filt-CDCl3_PROTON_01
Solvent	cdcl3
Number of Scans	8
Receiver Gain	40
Relaxation Delay	1.0000
Acquisition Date	2020-04-10T18:27:50
Spectrometer Frequency	399.97
Nucleus	1H

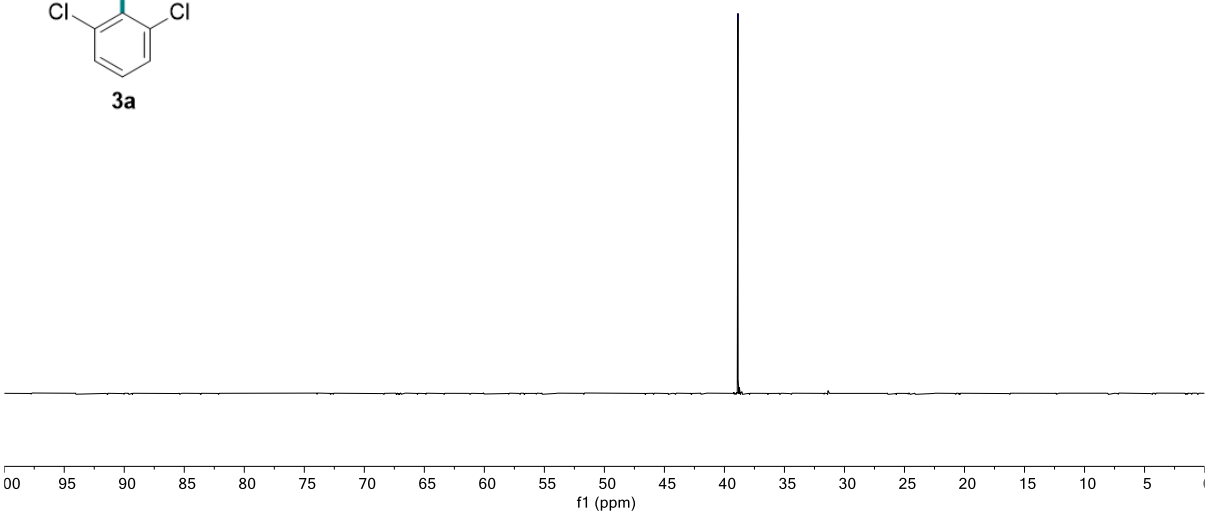


3a

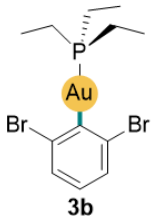
Title	FI-261-07-SiO2Filt-CDCl3_PHOSPHORUS_01
Solvent	cdcl3
Number of Scans	64
Receiver Gain	50
Relaxation Delay	1.0000
Acquisition Date	2020-04-10T18:31:01
Spectrometer Frequency	161.92
Nucleus	31P



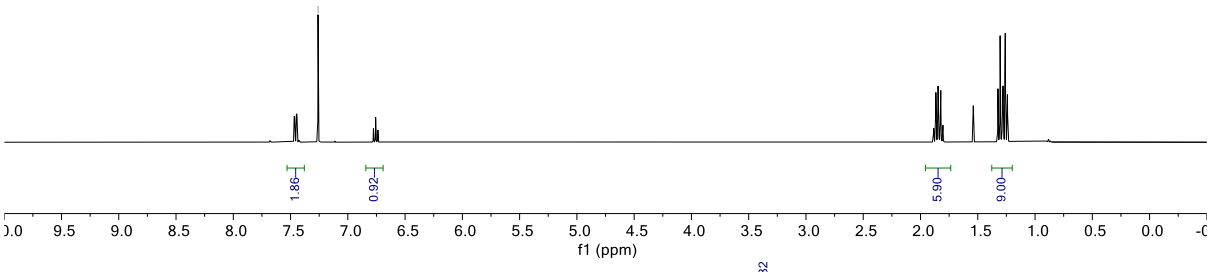
3a



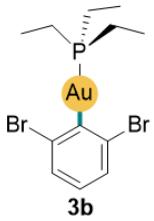
Title	FI-263-03-SiO2plug-CDCl3_PROTON_01
Solvent	cdcl3
Number of Scans	64
Receiver Gain	44
Relaxation Delay	1.0000
Acquisition Date	2020-04-10T19:49:54
Spectrometer Frequency	399.97
Nucleus	1H



3b

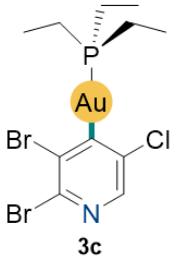


Title	FI-263-03-SiO2plug-CDCl3_PHOSPHORUS_01
Solvent	cdcl3
Number of Scans	128
Receiver Gain	50
Relaxation Delay	1.0000
Acquisition Date	2020-04-10T19:55:53
Spectrometer Frequency	161.92
Nucleus	31P

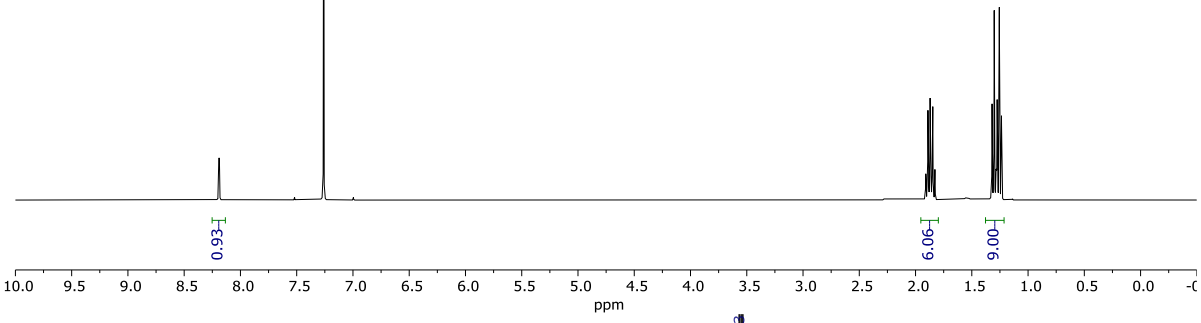


3b

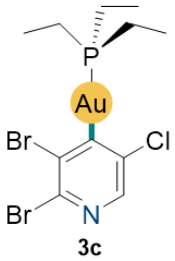
Title	ZXG-26-2-filter-2_PROTON_01
Acquisition Date	2020-04-20T12:30:42
Solvent	cdcl3
Number of Scans	32
Receiver Gain	48
Relaxation Delay	1.0000
Nucleus	1H
Spectrometer Frequency	399.97



3c

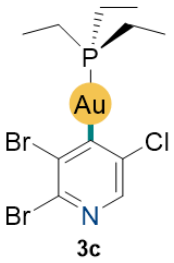


Title	ZXG-26-2-filter-SI_CARBON_01
Acquisition Date	2020-04-21T01:57:16
Solvent	cdcl3
Number of Scans	5000
Receiver Gain	30
Relaxation Delay	1.0000
Nucleus	13C
Spectrometer Frequency	100.58

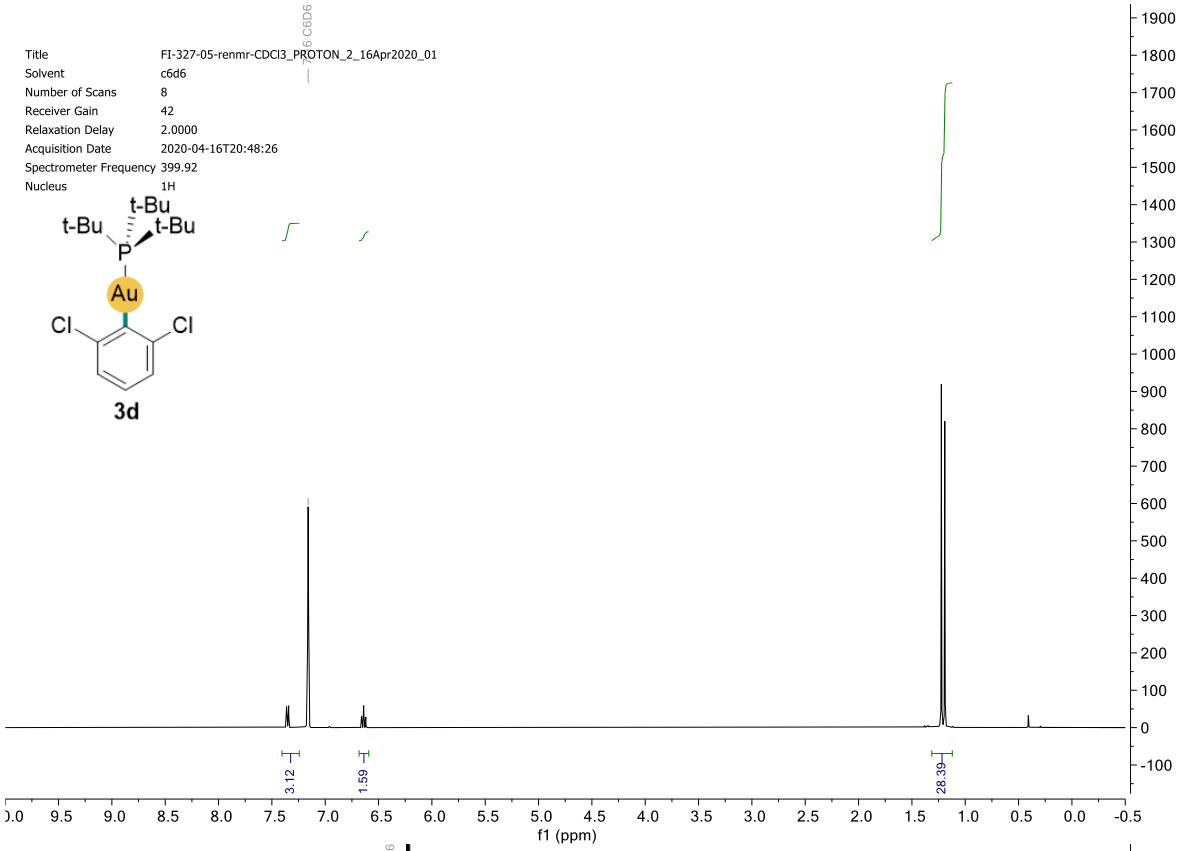


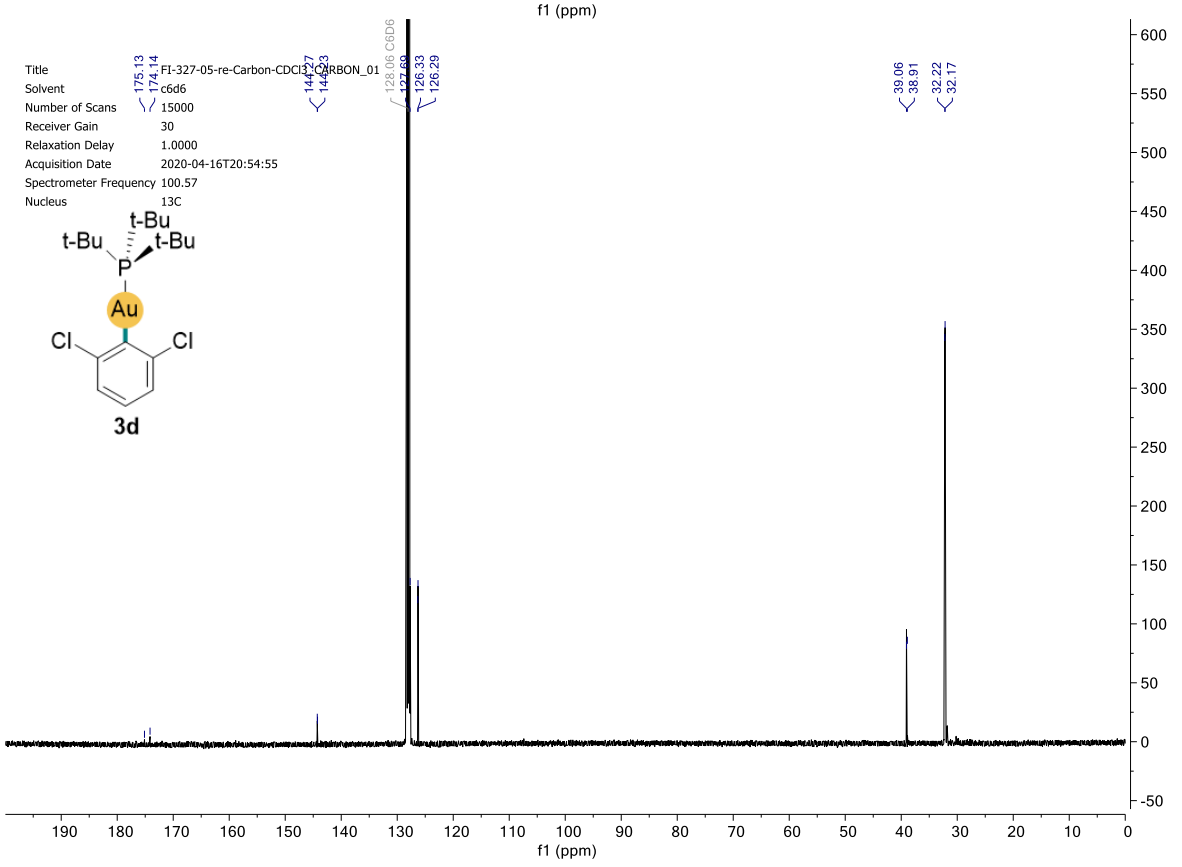
3c

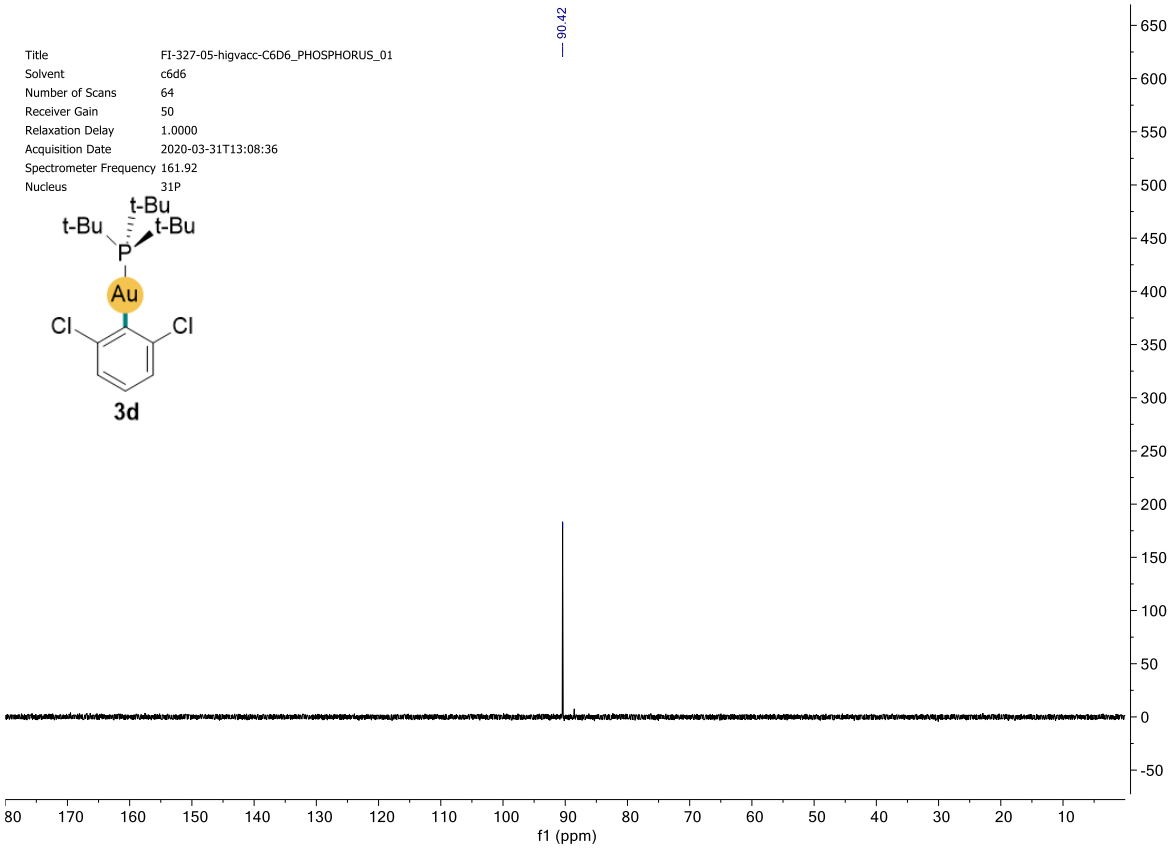
Title	ZXG-26-2-filter-2_PHOSPHORUS_01
Acquisition Date	2020-04-20T12:34:44
Solvent	cdcl3
Number of Scans	64
Receiver Gain	50
Relaxation Delay	1.0000
Nucleus	31P
Spectrometer Frequency	161.92



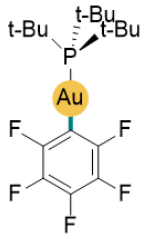
3c


Title FI-327-05-renmr-CDCl3_PROTON_2_16Apr2020_01
Solvent c6d6
Number of Scans 8
Receiver Gain 42
Relaxation Delay 2.0000
Acquisition Date 2020-04-16T20:48:26
Spectrometer Frequency 399.92
Nucleus 1H
t-Bu
t-Bu
t-Bu
P
Au
Cl
Cl
3d
C6D6
3.12
1.59
28.39
f1 (ppm)

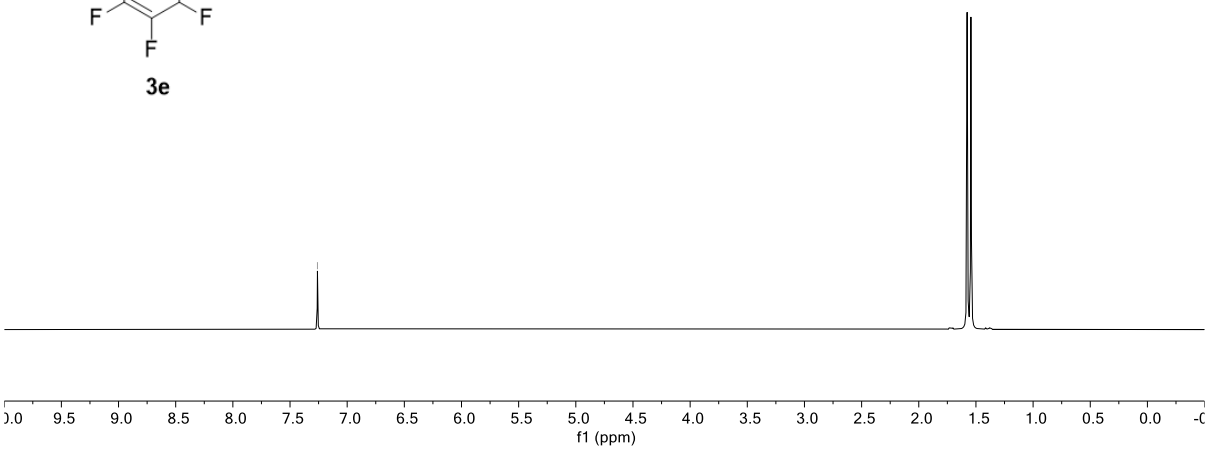

Title FI-327-05-re-Carbon-CDCl3_CARBON_01
Solvent c6d6
Number of Scans 15000
Receiver Gain 30
Relaxation Delay 1.0000
Acquisition Date 2020-04-16T20:54:55
Spectrometer Frequency 100.57
Nucleus 13C
175.13
174.14
144.27
146.23
128.06 C6D6
127.60
126.33
126.29
39.06
38.91
32.22
32.17
t-Bu
t-Bu
t-Bu
P
Au
Cl
Cl
3d
f1 (ppm)


Title FI-327-05-higvacc-C6D6_PHOSPHORUS_01
Solvent c6d6
Number of Scans 64
Receiver Gain 50
Relaxation Delay 1.0000
Acquisition Date 2020-03-31T13:08:36
Spectrometer Frequency 161.92
Nucleus 31P
t-Bu
t-Bu
t-Bu
P
Au
Cl
Cl
3d
90.42
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

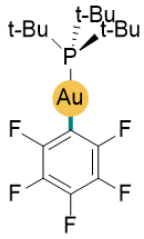
Title	FI-352-01-CDCl3_PROTON_01
Solvent	cdcl3
Number of Scans	8
Receiver Gain	32
Relaxation Delay	1.0000
Acquisition Date	2019-12-13T17:31:49
Spectrometer Frequency	399.97
Nucleus	1H



3e

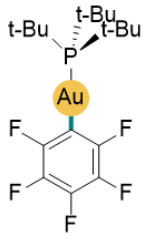


Title	FI-352-01-CDCl3_FLUORINE_01
Solvent	cdcl3
Number of Scans	16
Receiver Gain	52
Relaxation Delay	1.0000
Acquisition Date	2019-12-13T17:34:41
Spectrometer Frequency	376.31
Nucleus	19F



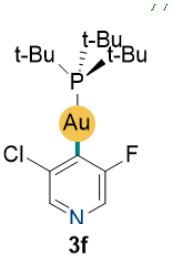
3e

Title	FI-352-01-CDCl3_PHOSPHORUS_01
Solvent	cdcl3
Number of Scans	64
Receiver Gain	50
Relaxation Delay	1.0000
Acquisition Date	2019-12-13T17:25:19
Spectrometer Frequency	161.92
Nucleus	31P

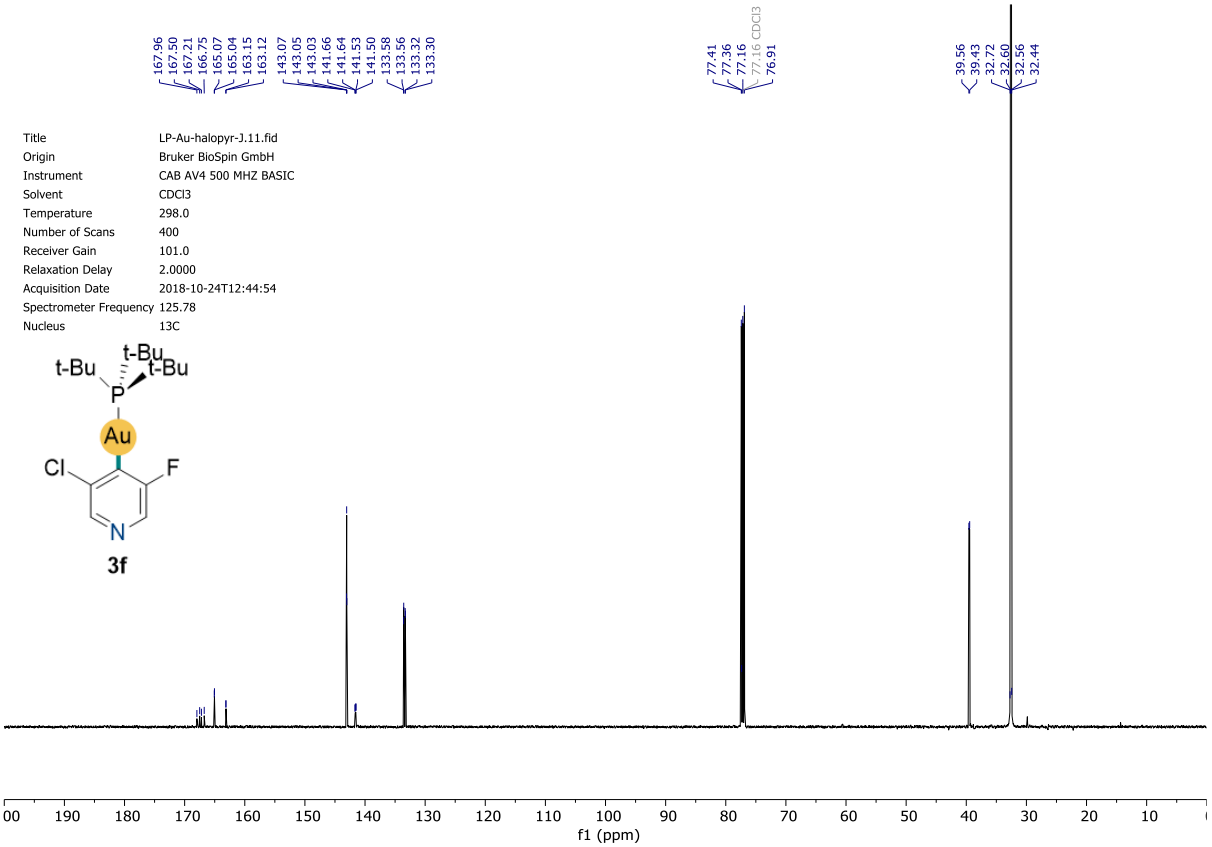


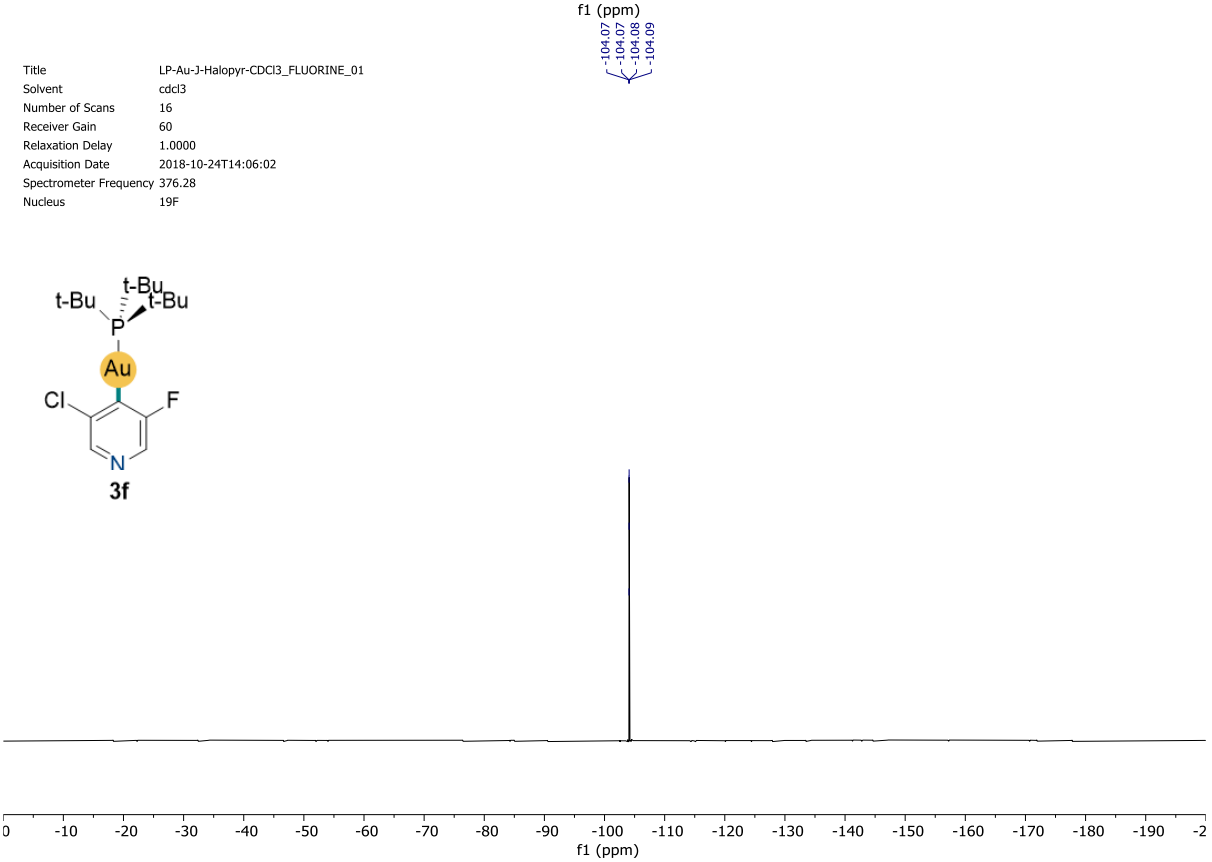
3e

Title	LP-Au-J-halopyr-column_PROTON_01
Solvent	cdcl3
Number of Scans	32
Receiver Gain	36
Relaxation Delay	4.0000
Acquisition Date	2018-10-24T11:31:51
Spectrometer Frequency	399.94
Nucleus	1H

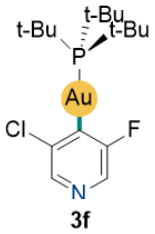


3f

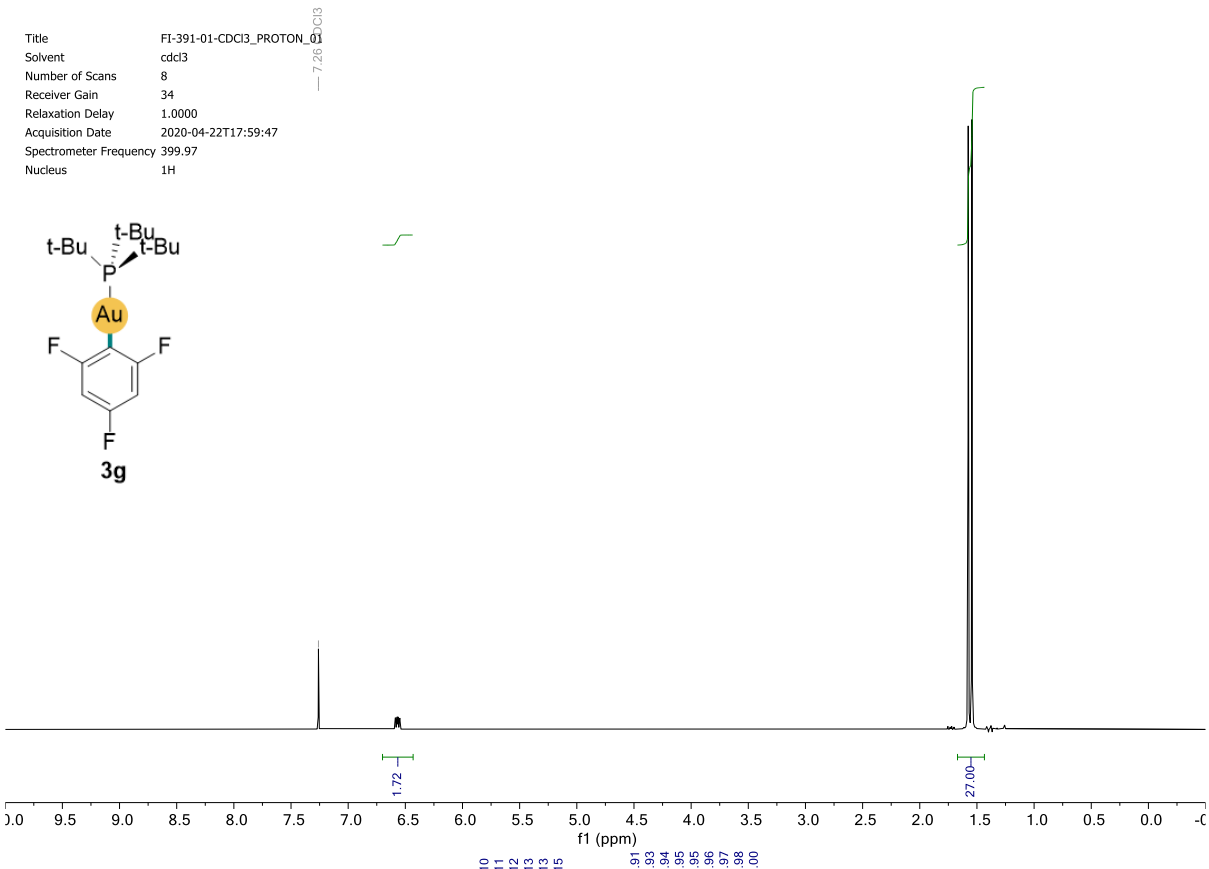

167.96
167.50
167.21
166.75
165.07
165.04
163.15
163.12
143.07
143.05
143.03
141.66
141.64
141.53
141.50
133.58
133.56
133.32
133.30
77.41
77.36
77.16
77.16 CDCl3
76.91
39.56
39.43
32.72
32.60
32.56
32.44
Title LP-Au-halopyr-J.11.fid
Origin Bruker BioSpin GmbH
Instrument CAB AV4 500 MHZ BASIC
Solvent CDCl3
Temperature 298.0
Number of Scans 400
Receiver Gain 101.0
Relaxation Delay 2.0000
Acquisition Date 2018-10-24T12:44:54
Spectrometer Frequency 125.78
Nucleus 13C
t-Bu
t-Bu
t-Bu
P
Au
Cl
F
N
3f
f1 (ppm)

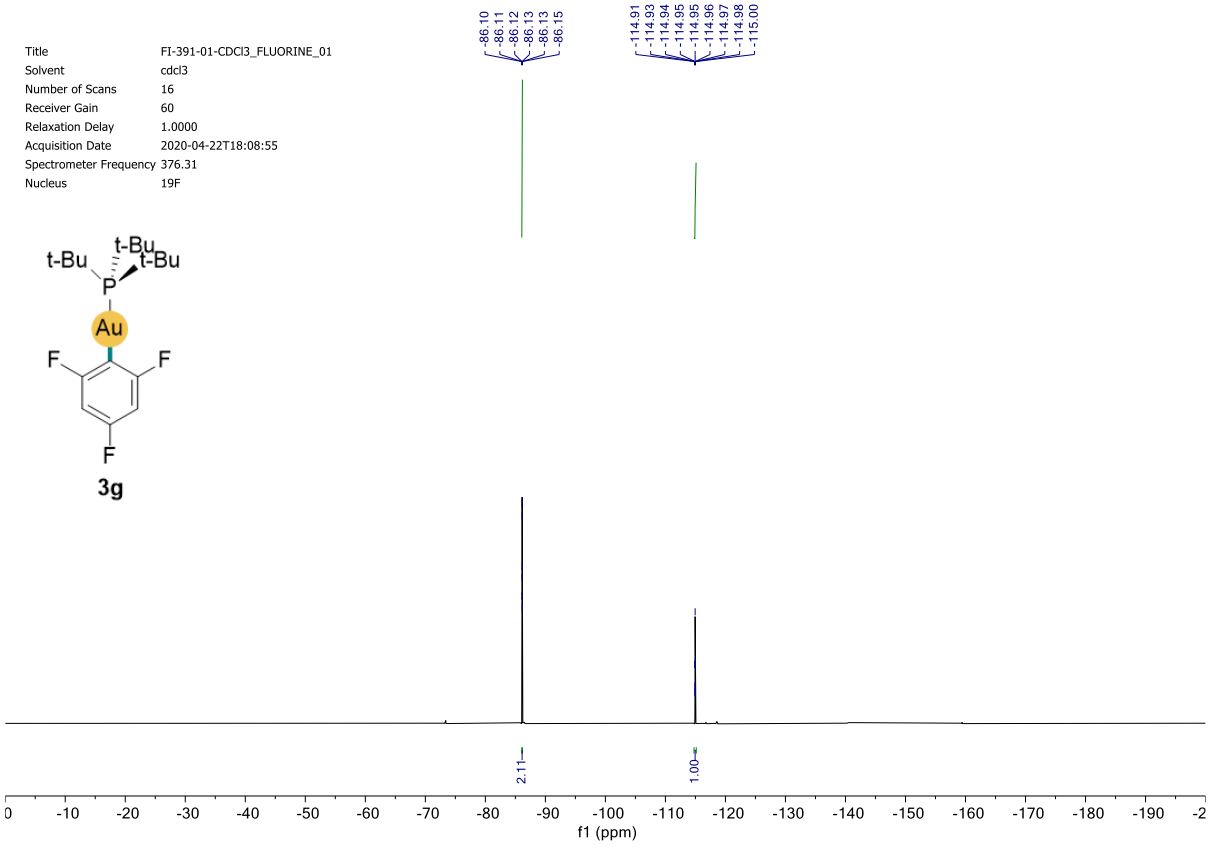

-104.07
-104.07
-104.08
-104.09
Title LP-Au-J-Halopyr-CDCl3_FLUORINE_01
Solvent cdcl3
Number of Scans 16
Receiver Gain 60
Relaxation Delay 1.0000
Acquisition Date 2018-10-24T14:06:02
Spectrometer Frequency 376.28
Nucleus 19F
t-Bu
t-Bu
t-Bu
P
Au
Cl
F
N
3f
f1 (ppm)

Title	LP-Au-J-halopyr-CDCl3_PHOSPHORUS_01
Solvent	cdcl3
Number of Scans	64
Receiver Gain	50
Relaxation Delay	1.0000
Acquisition Date	2018-10-24T13:32:41
Spectrometer Frequency	161.92
Nucleus	31P

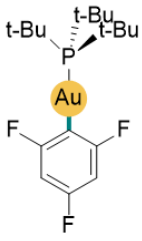


3f


Title FI-391-01-CDCl3_PROTON_01
Solvent cdcl3
Number of Scans 8
Receiver Gain 34
Relaxation Delay 1.0000
Acquisition Date 2020-04-22T17:59:47
Spectrometer Frequency 399.97
Nucleus 1H
7.26 CDCl3
t-Bu
t-Bu
t-Bu
P
Au
F
F
F
3g
1.72
27.00
f1 (ppm)


Title FI-391-01-CDCl3_FLUORINE_01
Solvent cdcl3
Number of Scans 16
Receiver Gain 60
Relaxation Delay 1.0000
Acquisition Date 2020-04-22T18:08:55
Spectrometer Frequency 376.31
Nucleus 19F
-86.10
-86.11
-86.12
-86.13
-86.13
-86.15
-114.91
-114.93
-114.94
-114.95
-114.95
-114.96
-114.97
-114.98
-115.00
t-Bu
t-Bu
t-Bu
P
Au
F
F
F
3g
2.11
1.00
f1 (ppm)

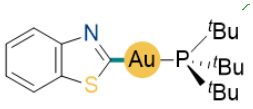
Title	FI-391-01-CDCl3_PHOSPHORUS_01
Solvent	cdcl3
Number of Scans	64
Receiver Gain	50
Relaxation Delay	1.0000
Acquisition Date	2020-04-22T18:02:51
Spectrometer Frequency	161.92
Nucleus	31P



3g

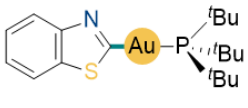
C-H Auration of heteroarenes (Scheme 3)

Title	FI-264-05-EtOAcflush-CDCl3_PROTON_01
Solvent	cdcl3
Number of Scans	8
Receiver Gain	42
Relaxation Delay	1.0000
Acquisition Date	2020-04-07T11:43:49
Spectrometer Frequency	399.97
Nucleus	1H

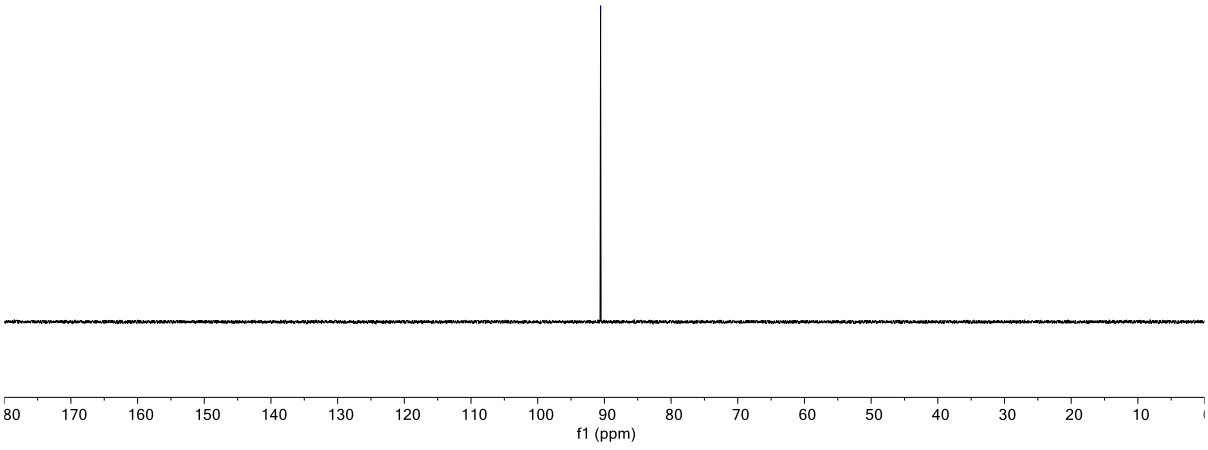


4a

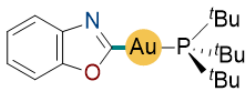
Title	FI-264-05-EtOAcflush-CDCl3_PHOSPHORUS_01
Solvent	cdcl3
Number of Scans	64
Receiver Gain	50
Relaxation Delay	1.0000
Acquisition Date	2020-04-07T11:46:46
Spectrometer Frequency	161.92
Nucleus	31P



4a

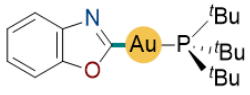


Title	ZXG-29-1-col-f-all-dry_PROTON_01
Acquisition Date	2020-04-23T09:31:51
Solvent	cdcl3
Number of Scans	32
Receiver Gain	38
Relaxation Delay	1.0000
Nucleus	1H
Spectrometer Frequency	399.97



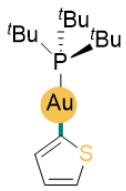
4b

Title	ZXG-29-1-col-f-all-dry_PHOSPHORUS_01
Acquisition Date	2020-04-23T09:36:21
Solvent	cdcl3
Number of Scans	64
Receiver Gain	50
Relaxation Delay	1.0000
Nucleus	31P
Spectrometer Frequency	161.92



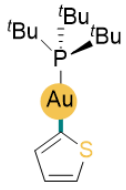
4b

Title	FI-326-03-longd1-CDCl3_PROTON_01
Solvent	cdcl3
Number of Scans	16
Receiver Gain	30
Relaxation Delay	25.0000
Acquisition Date	2019-10-18T14:15:50
Spectrometer Frequency	399.97
Nucleus	1H



4c

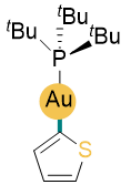
Title	FI-326-03-P-decoupl-CDCl3
Solvent	cdcl3
Number of Scans	32
Receiver Gain	30
Relaxation Delay	2.0000
Acquisition Date	2019-10-18T18:46:49
Decoupler nuclei	P31
Decoupler mode	nny
Spectrometer Frequency	399.97
Nucleus	1H



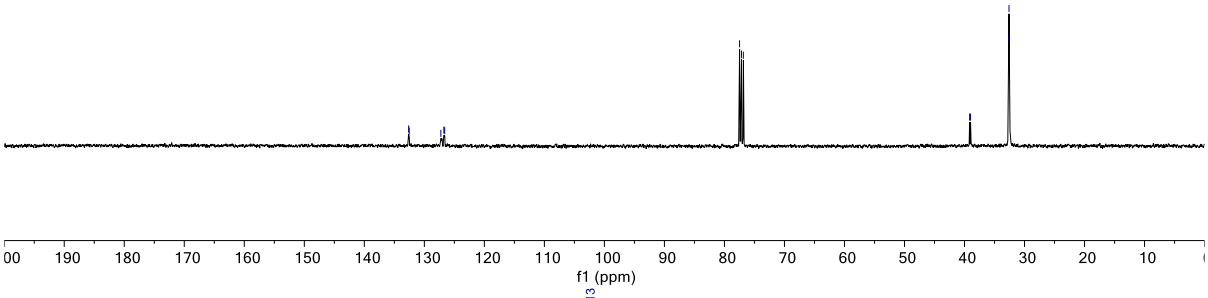
4c
31P Decoupled

Title	FI-326-03-carbon-CDCl3_CARBON_01
Solvent	cdcl3
Number of Scans	512
Receiver Gain	30
Relaxation Delay	1.0000
Acquisition Date	2019-10-18T14:30:15
Spectrometer Frequency	100.57
Nucleus	13C

132.62
132.52
127.25
126.75
126.61
77.48
77.16
77.16 CDCl3
76.85
39.15
38.99
32.63
32.59



4c

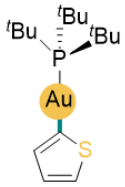


00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

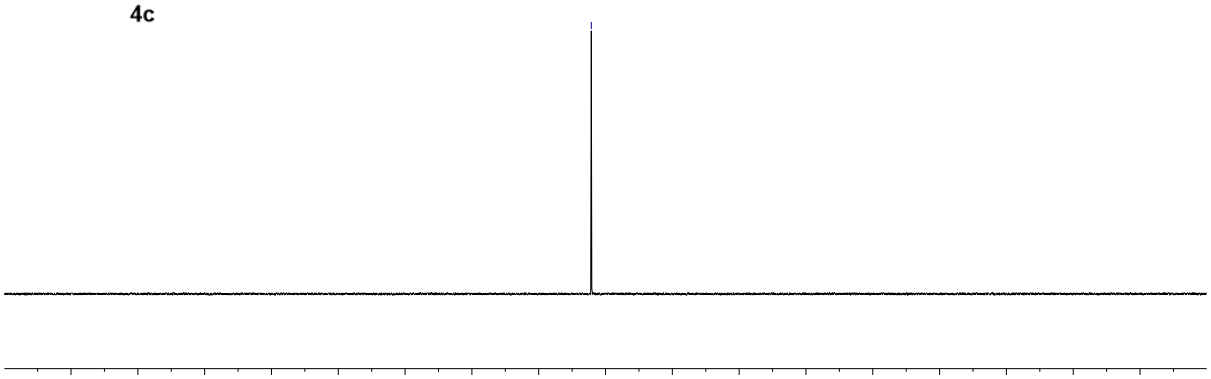
f1 (ppm)

92.13

Title	FI-326-03-longd1-CDCl3_PHOSPHORUS_01
Solvent	cdcl3
Number of Scans	64
Receiver Gain	50
Relaxation Delay	1.0000
Acquisition Date	2019-10-17T11:23:13
Spectrometer Frequency	161.92
Nucleus	31P



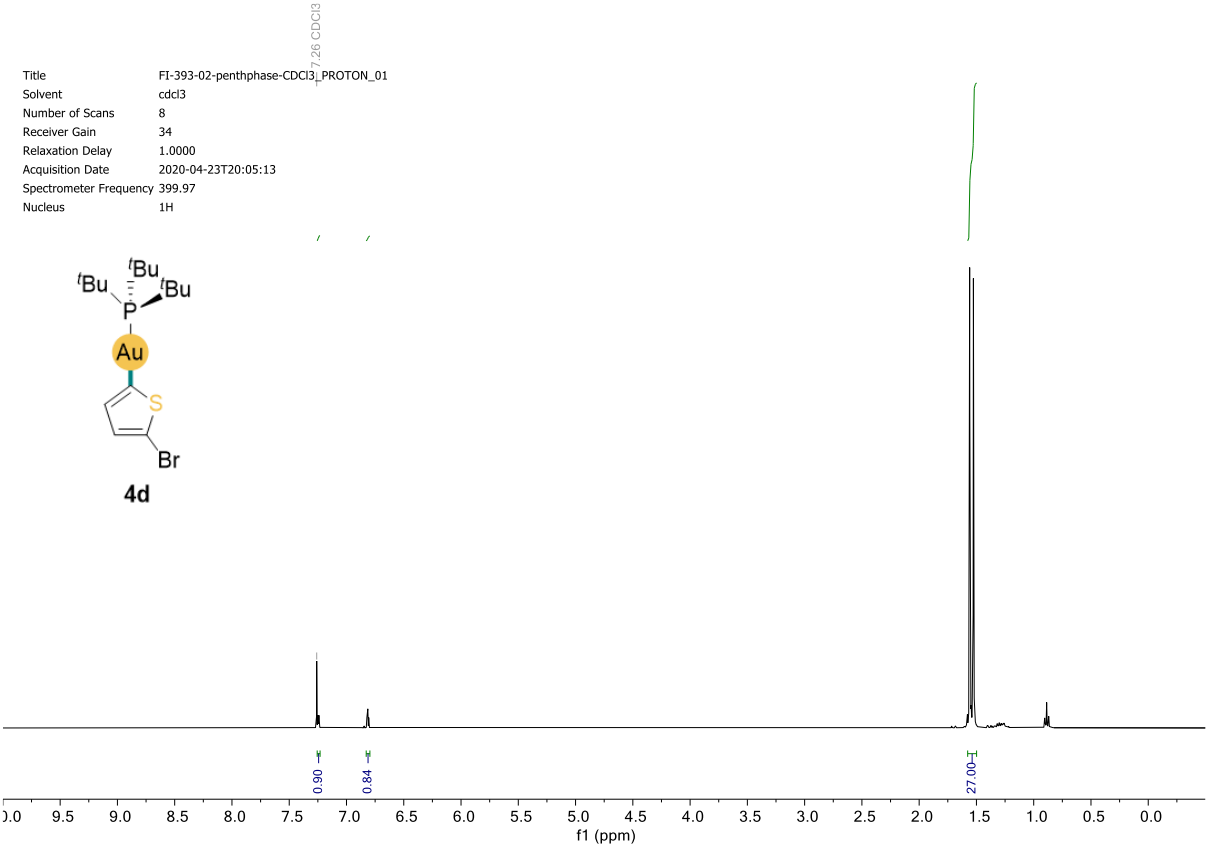
4c



170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

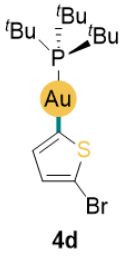
f1 (ppm)

Title	FI-393-02-penthphase-CDCl3_PROTON_01
Solvent	cdcl3
Number of Scans	8
Receiver Gain	34
Relaxation Delay	1.0000
Acquisition Date	2020-04-23T20:05:13
Spectrometer Frequency	399.97
Nucleus	1H



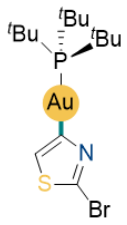
4d

Title	FI-393-02-penthphase-CDCl3_PHOSPHORUS_01
Solvent	cdcl3
Number of Scans	64
Receiver Gain	50
Relaxation Delay	1.0000
Acquisition Date	2020-04-23T20:07:50
Spectrometer Frequency	161.92
Nucleus	31P



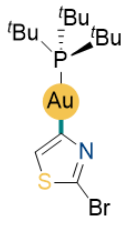
4d

Title	ZXG-30-1-col-f-all-dry_PROTON_01
Acquisition Date	2020-04-24T09:33:56
Solvent	cdcl3
Number of Scans	32
Receiver Gain	42
Relaxation Delay	1.0000
Nucleus	1H
Spectrometer Frequency	399.97

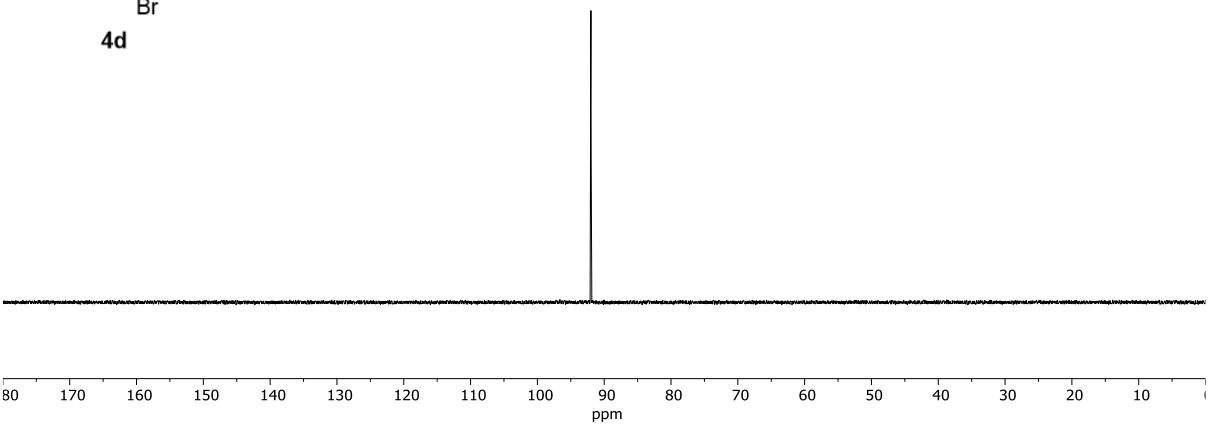


4d

Title	ZXG-30-1-col-f-all-dry_PHOSPHORUS_01
Acquisition Date	2020-04-24T09:38:26
Solvent	cdcl3
Number of Scans	64
Receiver Gain	50
Relaxation Delay	1.0000
Nucleus	31P
Spectrometer Frequency	161.92

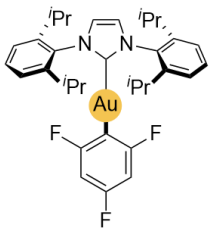


4d



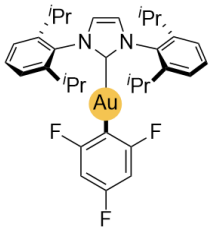
Au NHC complexes
(Scheme 4)

Title	FI-325-02-tbuok-CDCl3_PROTON_01
Solvent	cdcl3
Number of Scans	8
Receiver Gain	36
Relaxation Delay	1.0000
Acquisition Date	2019-09-03T19:39:19
Spectrometer Frequency	399.97
Nucleus	1H



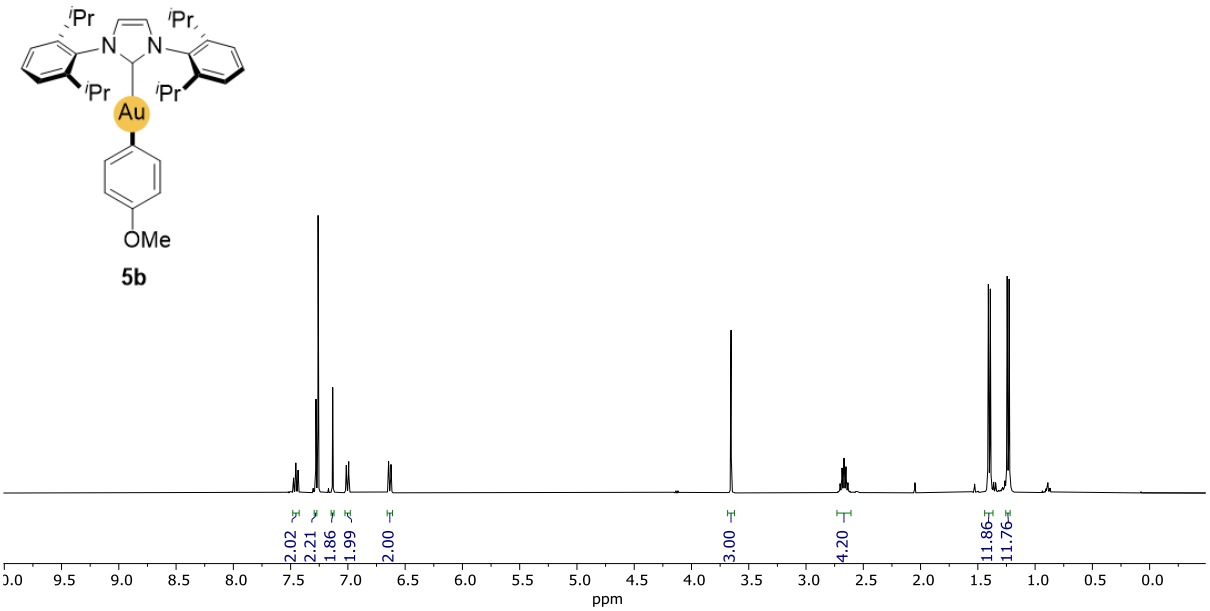
5a

Title	FI-325-02-tbuok-CDCl3_FLUORINE_01
Solvent	cdcl3
Number of Scans	16
Receiver Gain	60
Relaxation Delay	1.0000
Acquisition Date	2019-09-03T19:42:37
Spectrometer Frequency	376.31
Nucleus	19F



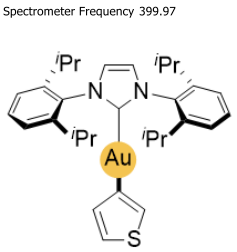
5a

Title	ZXG-23-3-filter_PROTON_01
Acquisition Date	2020-04-24T17:22:58
Solvent	cdcl3
Number of Scans	32
Receiver Gain	42
Relaxation Delay	1.0000
Nucleus	1H
Spectrometer Frequency	399.97



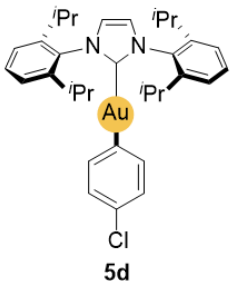
5b

Title	ZXG-3-5-filter_PROTON_01
Acquisition Date	2020-04-24T09:21:04
Solvent	cdcl3
Number of Scans	32
Receiver Gain	44
Relaxation Delay	1.0000
Nucleus	1H
Spectrometer Frequency	399.97

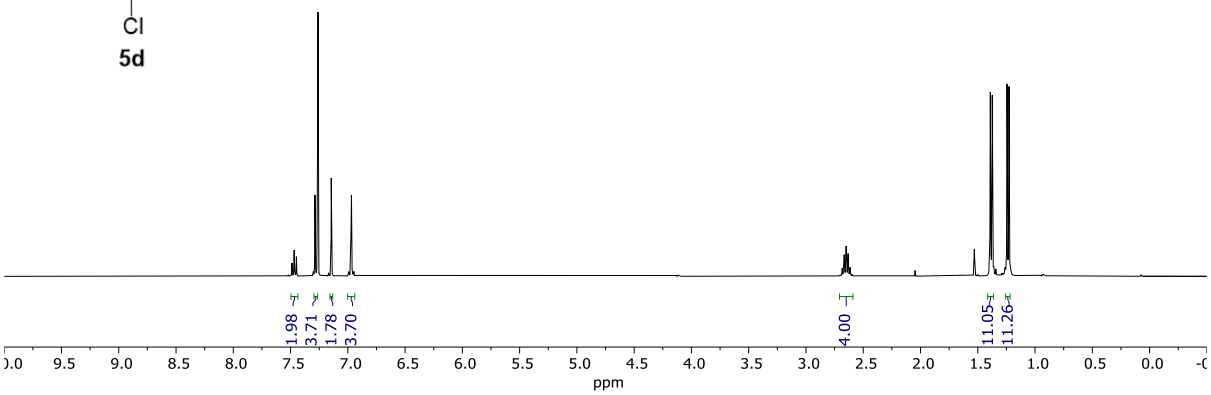


5c

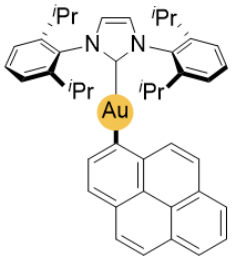
Title	ZXG-31-filter-SI_PROTON_01
Acquisition Date	2020-04-25T00:10:35
Solvent	cdcl3
Number of Scans	32
Receiver Gain	46
Relaxation Delay	1.0000
Nucleus	1H
Spectrometer Frequency	399.97



5d

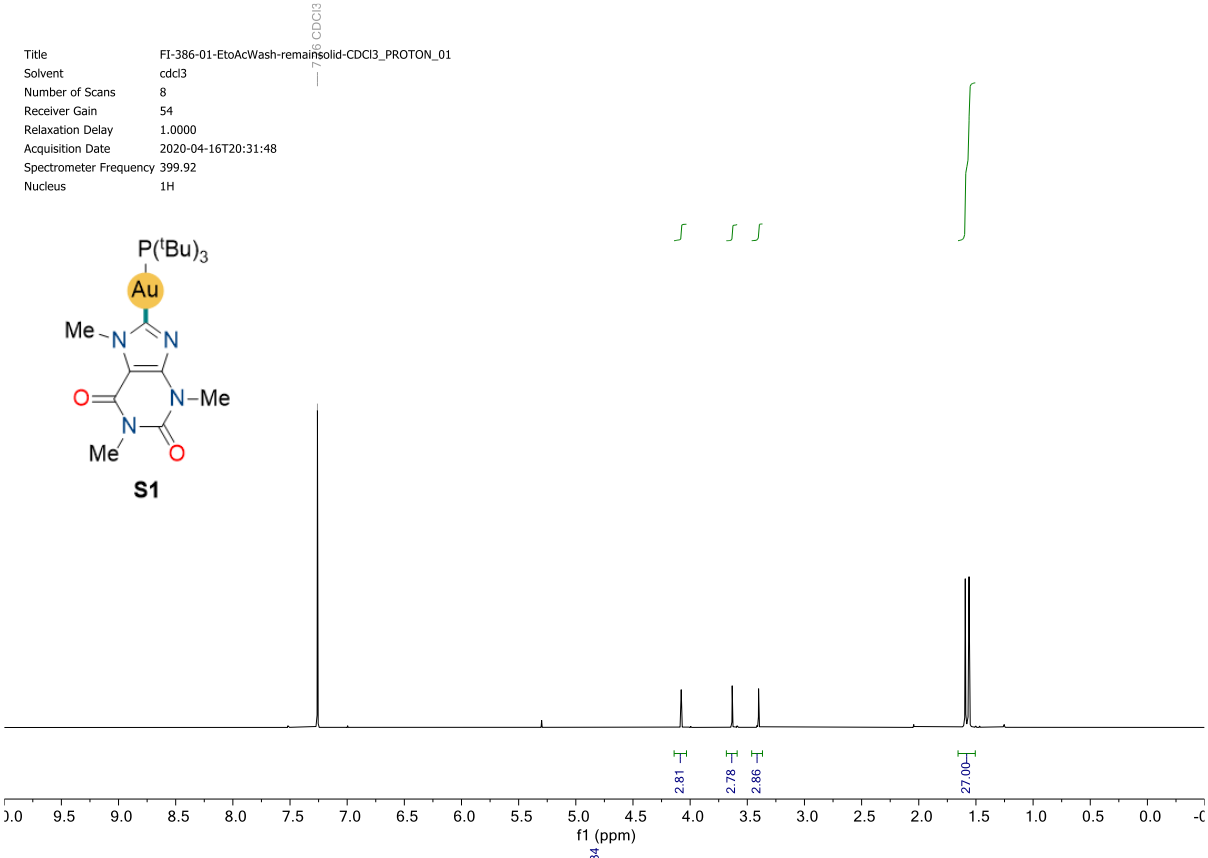


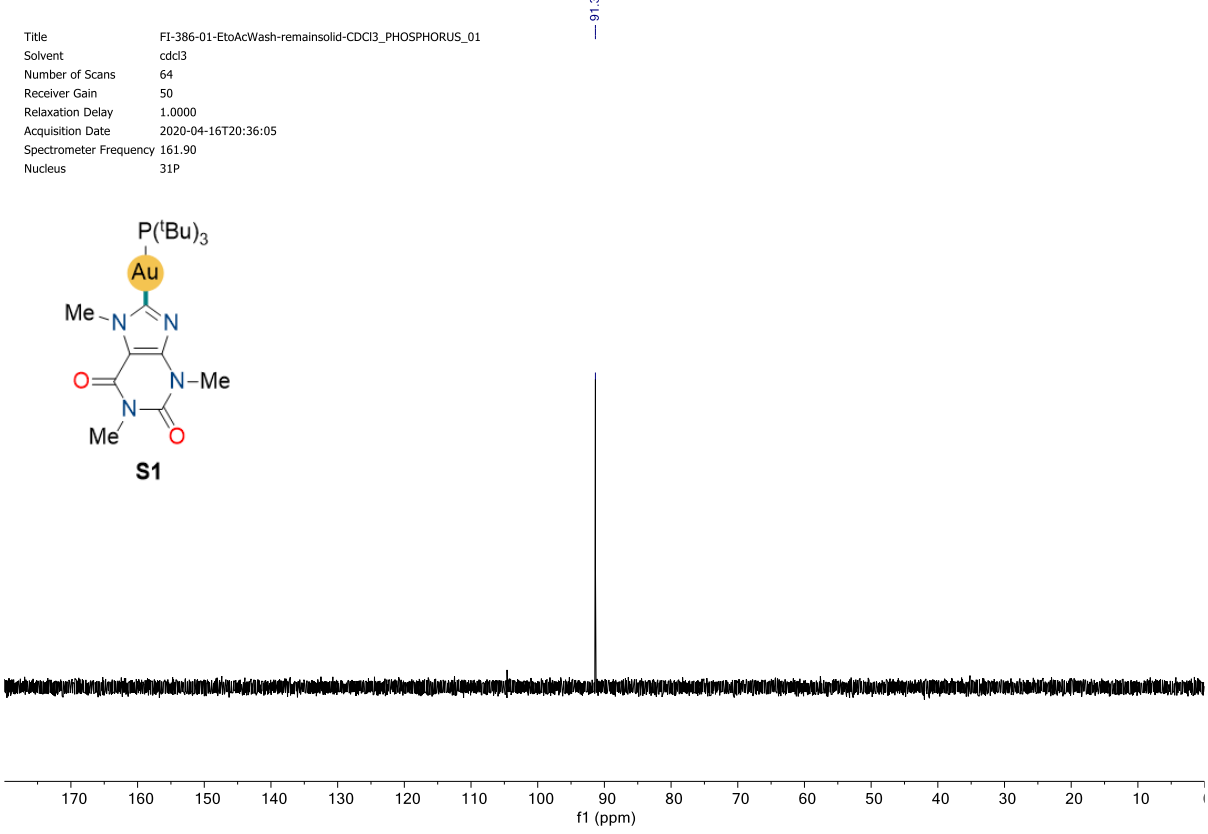
Title	FI-Au-O-pyrenen-NHC_PROTON_01
Solvent	cdcl3
Number of Scans	8
Receiver Gain	38
Relaxation Delay	1.0000
Acquisition Date	2018-05-14T23:26:18
Spectrometer Frequency	399.97
Nucleus	1H

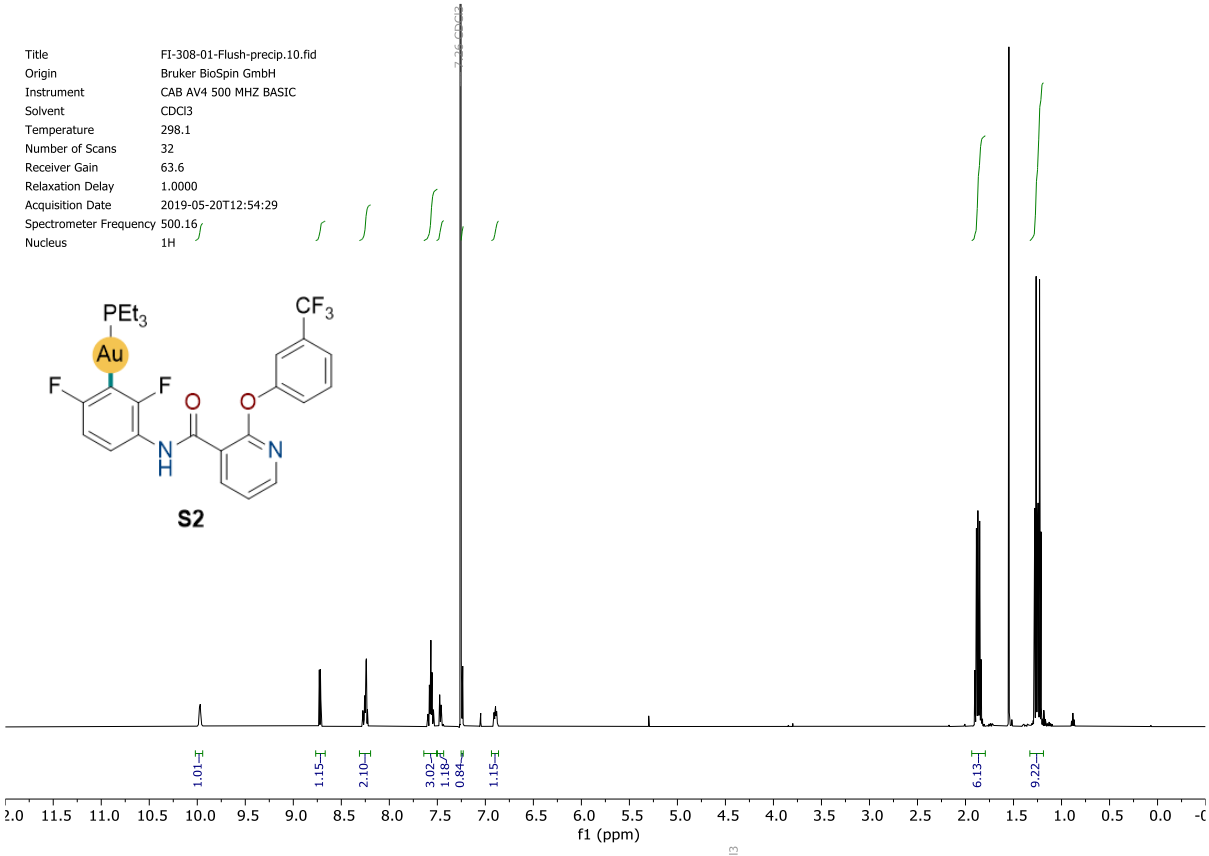


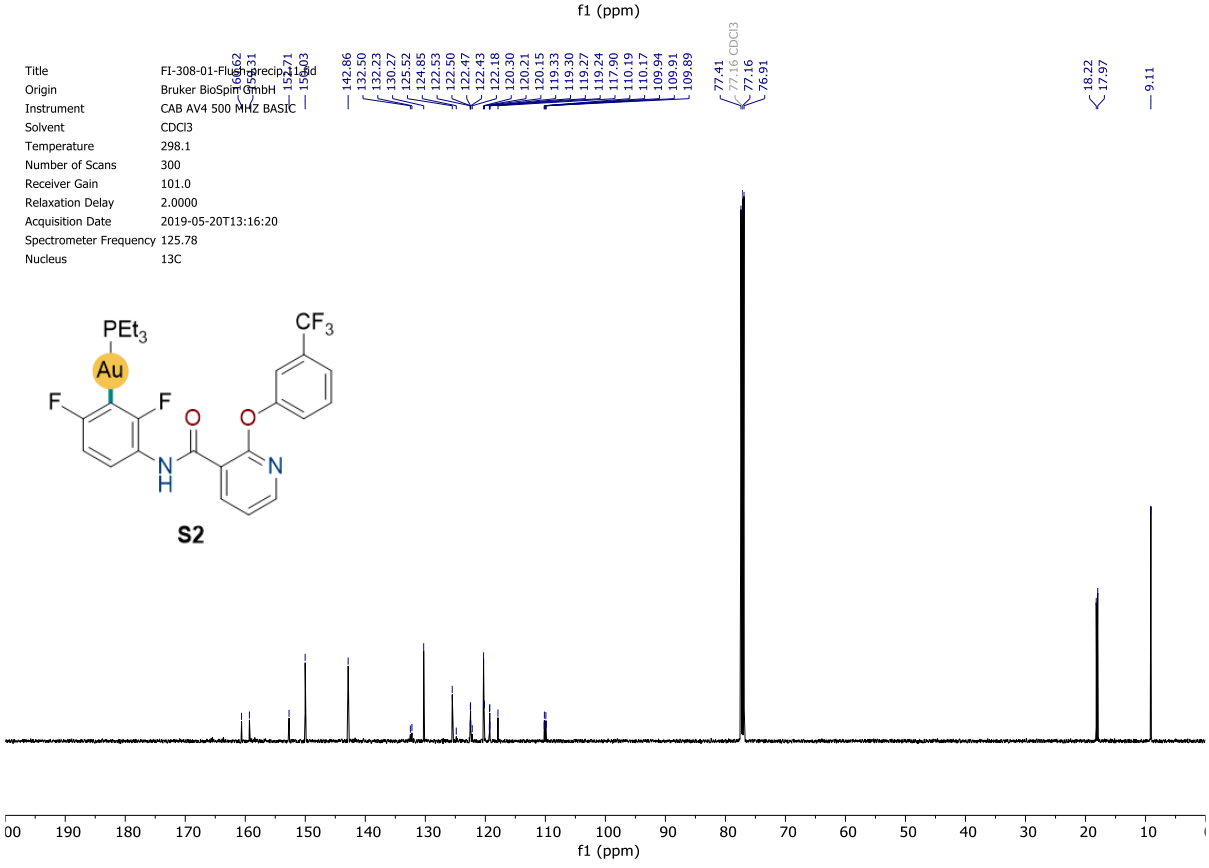
5e

Au(I) complexes of bioactive scaffolds (Figure 2)

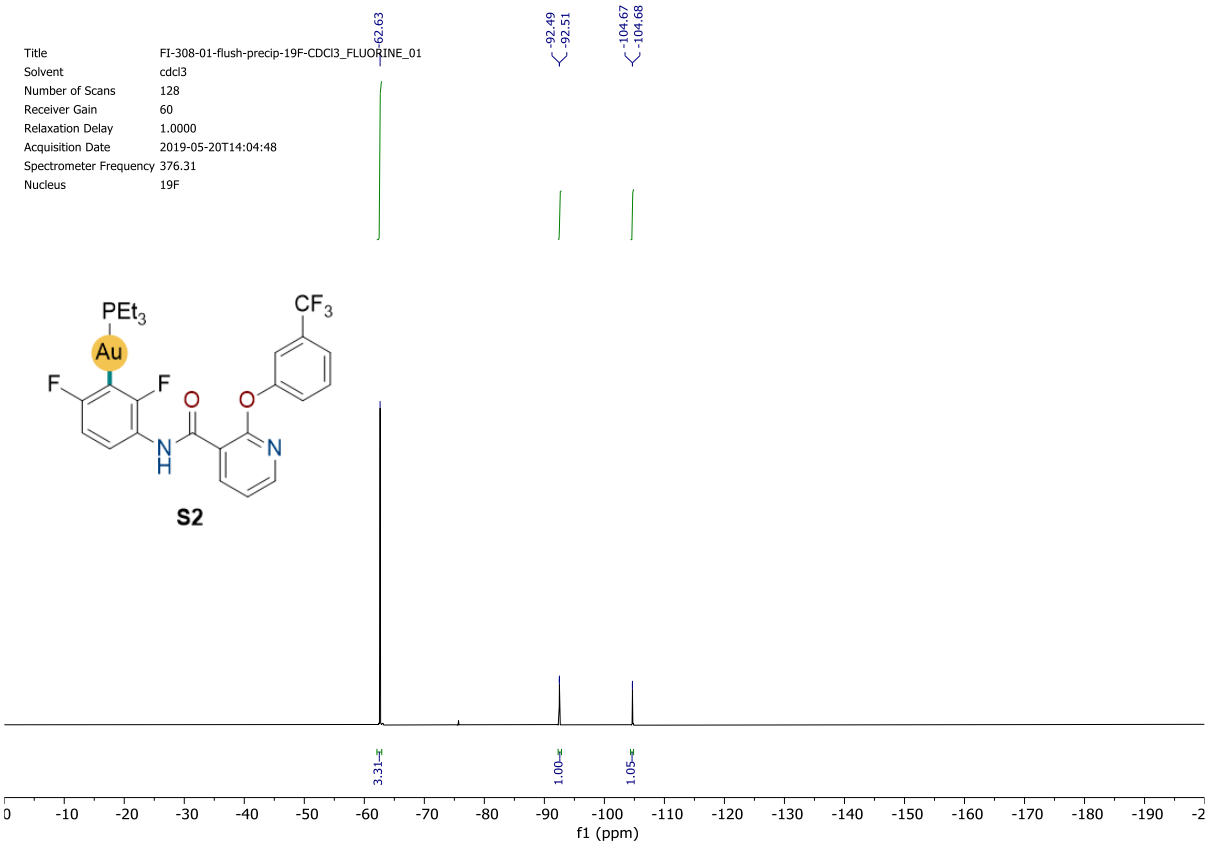

Title FI-386-01-EtoAcWash-remainsolid-CDCl3_PROTON_01
Solvent cdcl3
Number of Scans 8
Receiver Gain 54
Relaxation Delay 1.0000
Acquisition Date 2020-04-16T20:31:48
Spectrometer Frequency 399.92
Nucleus 1H
7.26 CDCl3
P(tBu)3
Au
Me
N
N
O
N–Me
N
Me
O
S1
2.81
2.78
2.86
27.00
f1 (ppm)


91.34
Title FI-386-01-EtoAcWash-remainsolid-CDCl3_PHOSPHORUS_01
Solvent cdcl3
Number of Scans 64
Receiver Gain 50
Relaxation Delay 1.0000
Acquisition Date 2020-04-16T20:36:05
Spectrometer Frequency 161.90
Nucleus 31P
P(tBu)3
Au
Me
N
N
O
N–Me
N
Me
O
S1
f1 (ppm)


Title FI-308-01-Flush-precip.10.fid
Origin Bruker BioSpin GmbH
Instrument CAB AV4 500 MHZ BASIC
Solvent CDCl3
Temperature 298.1
Number of Scans 32
Receiver Gain 63.6
Relaxation Delay 1.0000
Acquisition Date 2019-05-20T12:54:29
Spectrometer Frequency 500.16
Nucleus 1H
7.26 CDCl3
PEt3
Au
F
F
O
O
N
H
N
CF3
S2
1.01
1.15
2.10
3.02
1.18
0.84
1.15
6.13
9.22
f1 (ppm)

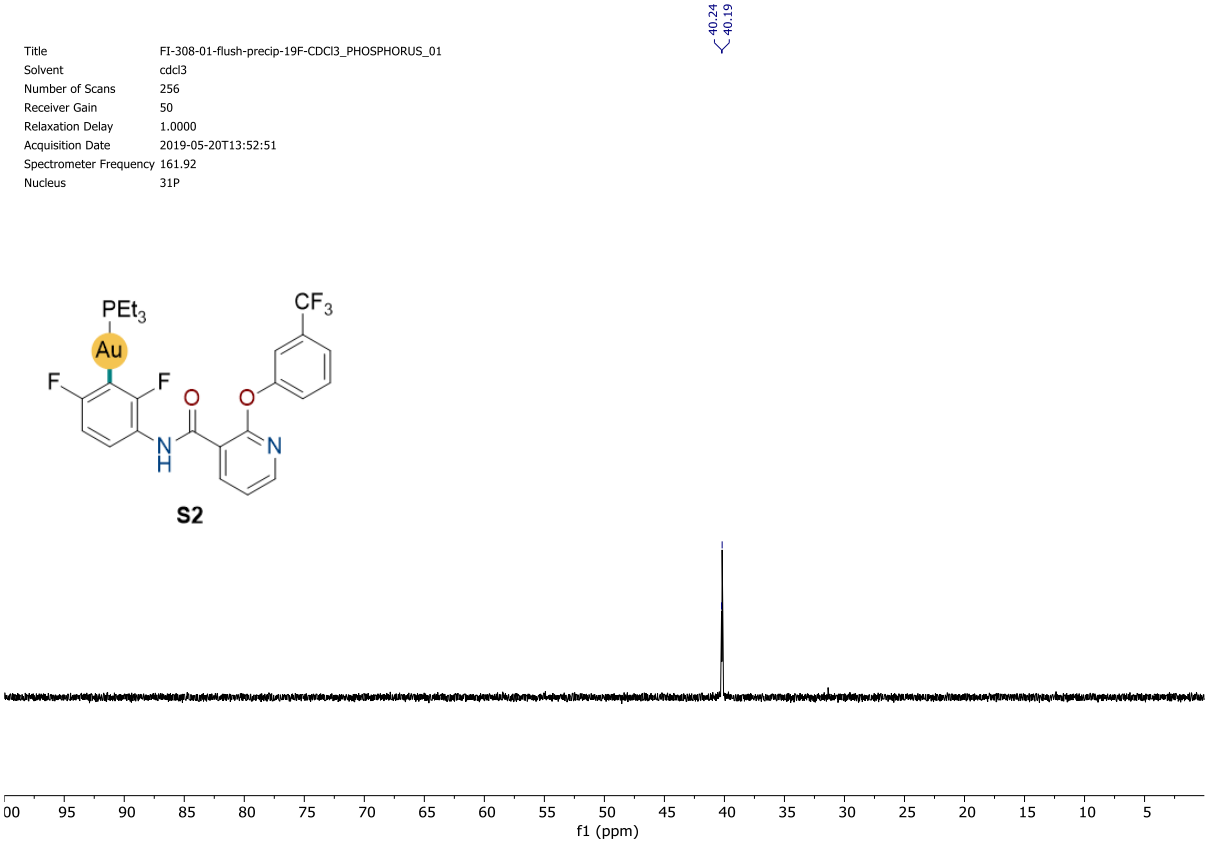

Title FI-308-01-Flush-precip.11.fid
Origin Bruker BioSpin GmbH
Instrument CAB AV4 500 MHZ BASIC
Solvent CDCl3
Temperature 298.1
Number of Scans 300
Receiver Gain 101.0
Relaxation Delay 2.0000
Acquisition Date 2019-05-20T13:16:20
Spectrometer Frequency 125.78
Nucleus 13C
159.62
159.31
157.71
157.03
142.86
132.50
132.23
130.27
125.52
124.85
122.53
122.50
122.47
122.43
122.18
120.30
120.21
120.15
119.33
119.30
119.27
119.24
117.90
110.19
110.17
109.94
109.91
109.89
77.41
77.16 CDCl3
76.91
18.22
17.97
9.11
PEt3
Au
F
F
O
O
N
H
N
CF3
S2
f1 (ppm)

Title	FI-308-01-flush-precip-19F-CDCl3_FLUORINE_01
Solvent	cdcl3
Number of Scans	128
Receiver Gain	60
Relaxation Delay	1.0000
Acquisition Date	2019-05-20T14:04:48
Spectrometer Frequency	376.31
Nucleus	19F

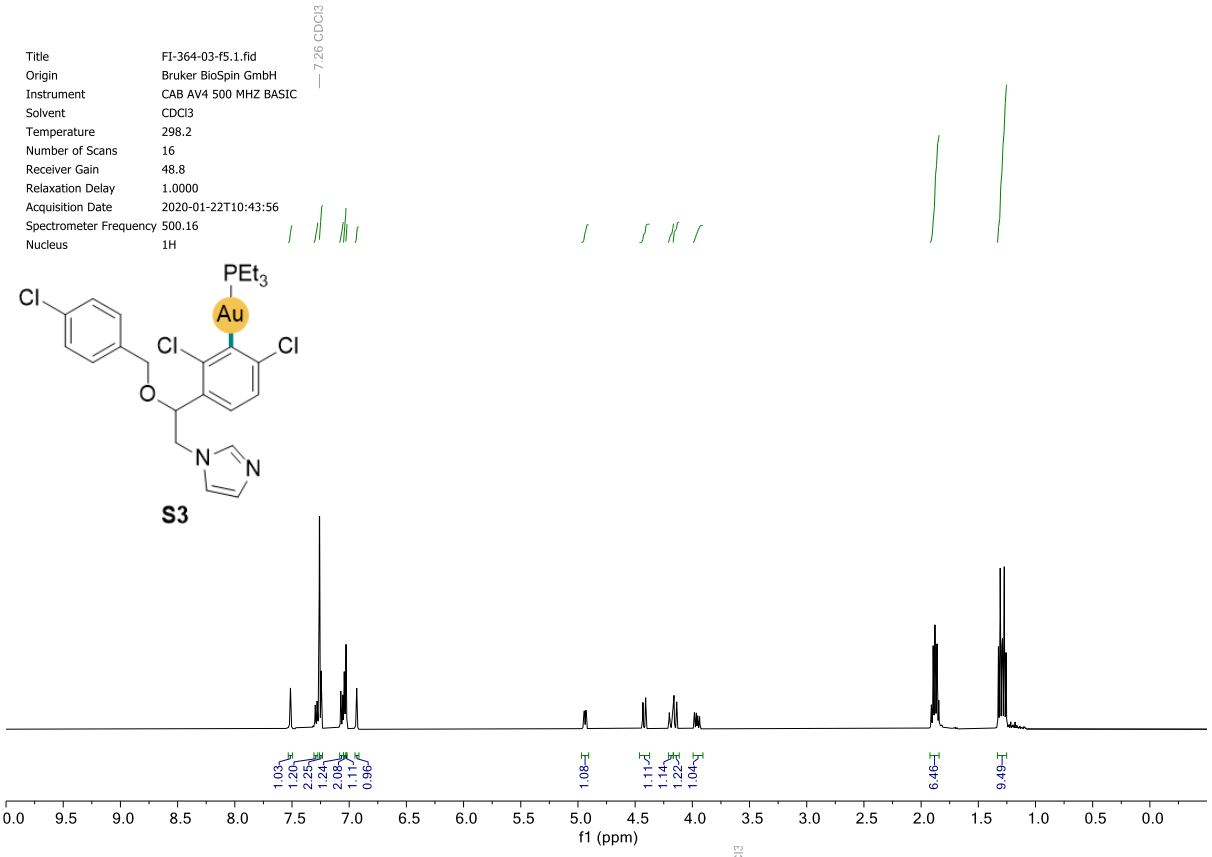


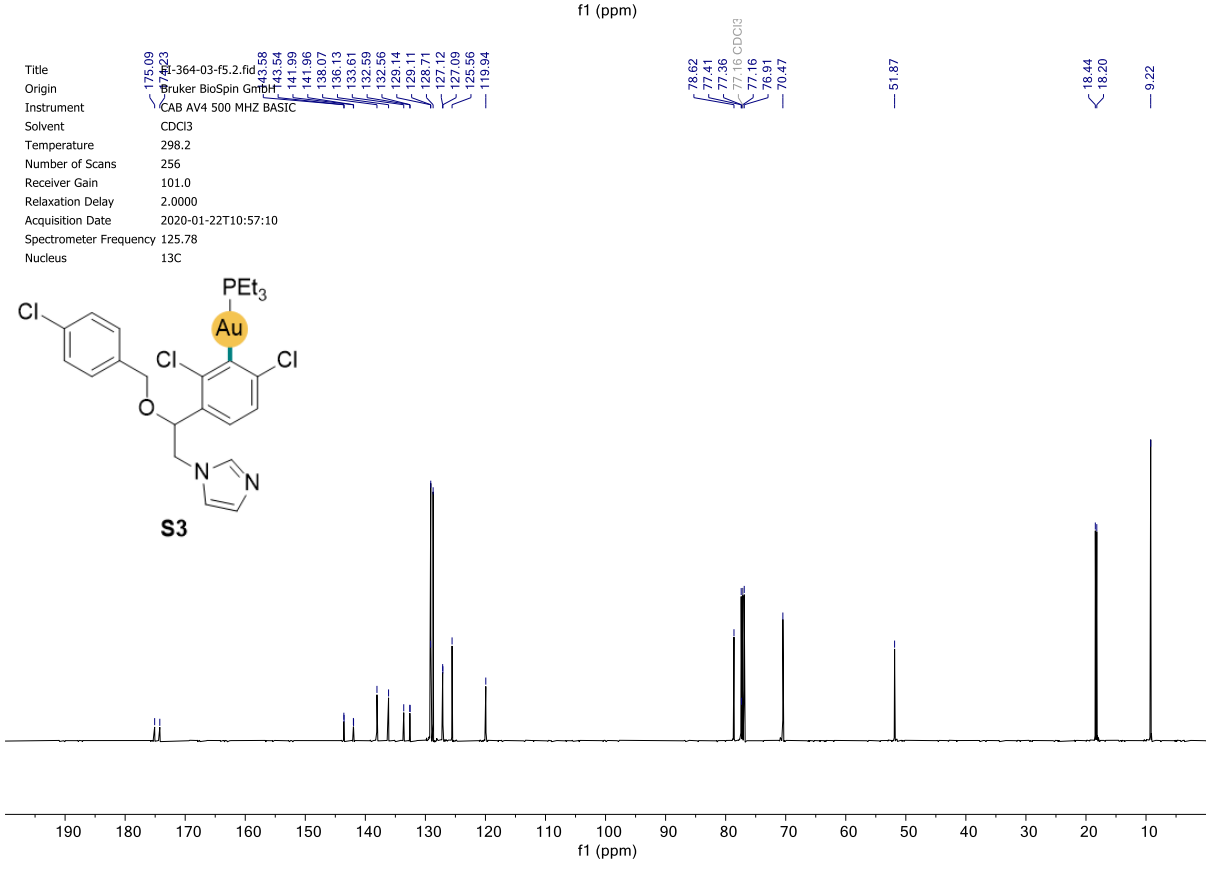
S2

Title	FI-308-01-flush-precip-19F-CDCl3_PHOSPHORUS_01
Solvent	cdcl3
Number of Scans	256
Receiver Gain	50
Relaxation Delay	1.0000
Acquisition Date	2019-05-20T13:52:51
Spectrometer Frequency	161.92
Nucleus	31P

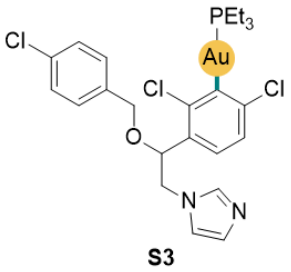


S2


Title FI-364-03-f5.1.fid
Origin Bruker BioSpin GmbH
Instrument CAB AV4 500 MHZ BASIC
Solvent CDCl3
Temperature 298.2
Number of Scans 16
Receiver Gain 48.8
Relaxation Delay 1.0000
Acquisition Date 2020-01-22T10:43:56
Spectrometer Frequency 500.16
Nucleus 1H
7.26 CDCl3
PEt3
Au
Cl
Cl
Cl
O
N
N
S3
1.03
1.20
2.25
1.24
2.08
1.11
0.96
1.08
1.11
1.14
1.22
1.04
6.46
9.49
f1 (ppm)


Title FI-364-03-f5.2.fid
Origin Bruker BioSpin GmbH
Instrument CAB AV4 500 MHZ BASIC
Solvent CDCl3
Temperature 298.2
Number of Scans 256
Receiver Gain 101.0
Relaxation Delay 2.0000
Acquisition Date 2020-01-22T10:57:10
Spectrometer Frequency 125.78
Nucleus 13C
175.09
77.23
143.58
143.54
141.99
141.96
138.07
136.13
133.61
132.59
132.56
129.14
129.11
128.71
127.12
127.09
125.56
119.94
78.62
77.41
77.36
77.16 CDCl3
77.16
76.91
70.47
51.87
18.44
18.20
9.22
PEt3
Au
Cl
Cl
Cl
O
N
N
S3
f1 (ppm)

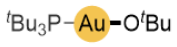
Title	FI-364-03-F5-CDCl3_PHOSPHORUS_01
Solvent	cdcl3
Number of Scans	64
Receiver Gain	50
Relaxation Delay	1.0000
Acquisition Date	2020-01-22T09:54:40
Spectrometer Frequency	161.92
Nucleus	31P



S3

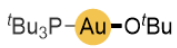
Mechanistic investigation (Scheme 7 and SI)

Title	FI-369-09-benzeneLAG-C6D6_PROTON_01
Solvent	c6d6
Number of Scans	8
Receiver Gain	38
Relaxation Delay	1.0000
Acquisition Date	2020-05-15T19:23:08
Spectrometer Frequency	399.97
Nucleus	1H



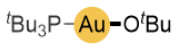
6

Title	FI-369-09-benzeneLAG-C6D6_CARBON_01
Solvent	c6d6
Number of Scans	10000
Receiver Gain	30
Relaxation Delay	1.0000
Acquisition Date	2020-05-07T19:53:23
Spectrometer Frequency	100.57
Nucleus	13C

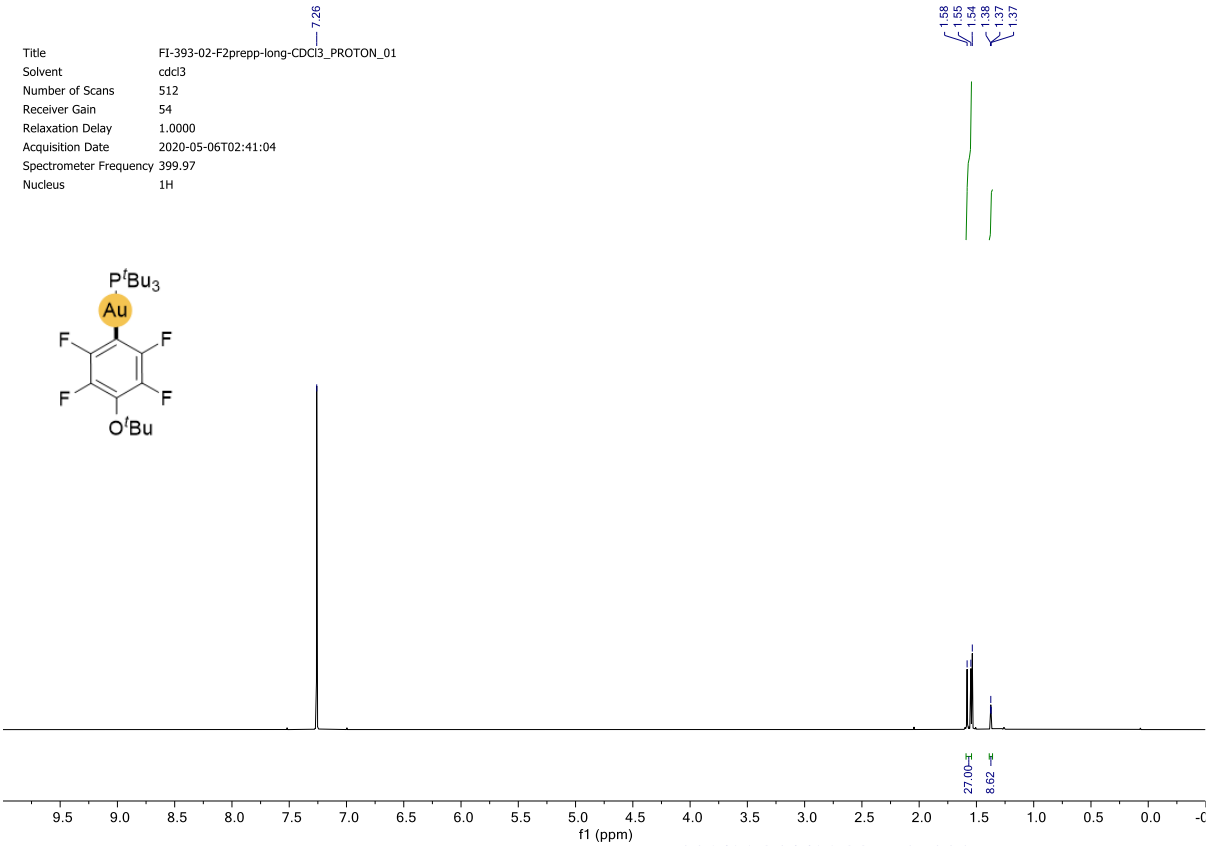


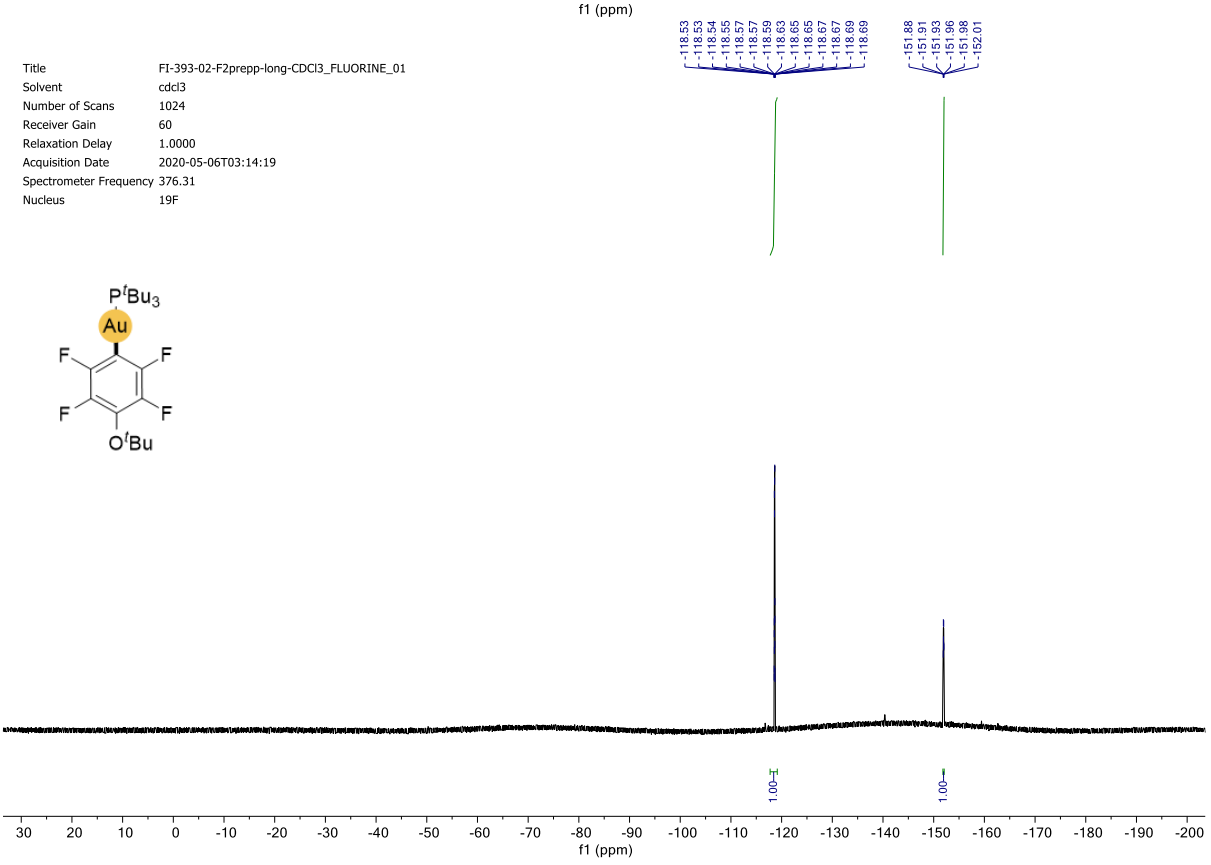
6

Title	FI-369-09-0_1mLC6H6add-C6D6_PHOSPHORUS_01
Solvent	c6d6
Number of Scans	128
Receiver Gain	50
Relaxation Delay	1.0000
Acquisition Date	2020-05-07T19:39:29
Spectrometer Frequency	161.92
Nucleus	31P



6


7.26
1.58
1.55
1.54
1.38
1.37
1.37
Title FI-393-02-F2prepp-long-CDCl3_PROTON_01
Solvent cdcl3
Number of Scans 512
Receiver Gain 54
Relaxation Delay 1.0000
Acquisition Date 2020-05-06T02:41:04
Spectrometer Frequency 399.97
Nucleus 1H
P^{t}Bu$_3$
Au
F
F
F
F
O^{t}Bu
27.00
8.62
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


-118.53
-118.53
-118.54
-118.55
-118.57
-118.57
-118.59
-118.63
-118.65
-118.65
-118.67
-118.67
-118.69
-118.69
-151.88
-151.91
-151.93
-151.96
-151.98
-152.01
Title FI-393-02-F2prepp-long-CDCl3_FLUORINE_01
Solvent cdcl3
Number of Scans 1024
Receiver Gain 60
Relaxation Delay 1.0000
Acquisition Date 2020-05-06T03:14:19
Spectrometer Frequency 376.31
Nucleus 19F
P^{t}Bu$_3$
Au
F
F
F
F
O^{t}Bu
1.00
1.00
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

Title	FI-393-02-F2prepp-long-CDCl3_PHOSPHORUS_01
Solvent	cdcl3
Number of Scans	4096
Receiver Gain	50
Relaxation Delay	1.0000
Acquisition Date	2020-05-06T03:46:47
Spectrometer Frequency	161.92
Nucleus	31P