

## SUPPORTING INFORMATION

### Hemilabile MIC<sup>^</sup>N ligands allow oxidant-free Au(I)/Au(III) arylation-lactonization of $\gamma$ -alkenoic acids

Pau Font,<sup>†</sup> Hugo Valdés,<sup>†,\*</sup> Gregorio Guisado-Barrios,<sup>‡,\*</sup> Xavi Ribas<sup>†,\*</sup>

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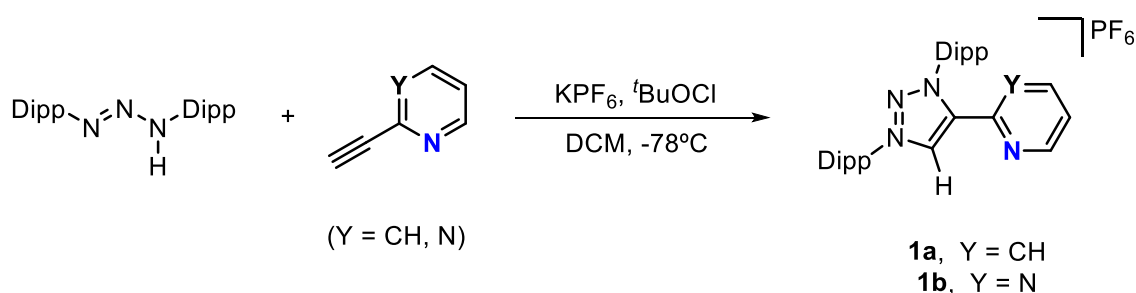
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## 1. General considerations

All reagents and solvents were purchased from Sigma Aldrich, Fischer Scientific, TCI or Fluorochem and were used without further purification. *Tert*-butyl hypochlorite<sup>1</sup> and 1,3-bis(2,6-diisopropylphenyl)triaz-1-ene<sup>2</sup> were prepared following reported methods. NMR spectra were recorded on Bruker spectrometers operating at 400 MHz (<sup>1</sup>H NMR) and 101 MHz (<sup>13</sup>C{<sup>1</sup>H} NMR), and referenced to residual solvent, ( $\delta$  in ppm and *J* in hertz). <sup>1</sup>H NMR spectra recorded in CD<sub>2</sub>Cl<sub>2</sub> are referenced at 5.32 ppm and those recorded in CDCl<sub>3</sub>, at 7.26 ppm. Quantification of reaction yields was done by integration of the NMR signals, using an internal standard. High resolution mass spectra (HRMS) were recorded on a Bruker MicroTOF-Q IITM instrument using ESI source at Serveis Tècnics de Recerca, University of Girona. For reactions carried out under inert atmosphere, a N<sub>2</sub> drybox with O<sub>2</sub> and H<sub>2</sub>O concentrations <1 ppm was employed. The reaction carried out under blue LED irradiation was performed in an in-house created photoreactor, which consists in an aluminum block with 16 holes for 20 mL vials, at the bottom of each hole is located a LED irradiation source. The aluminum block is over an orbital shaker and is also equipped with a refrigeration system to control the temperature of the photoreactor.

## 2. Synthesis of triazolium salts **1a** and **1b**



**Scheme S1.** Synthesis of triazolium salts **1a** and **1b**.

The triazolium salts were prepared by adapting a reported method in the literature.<sup>3</sup>

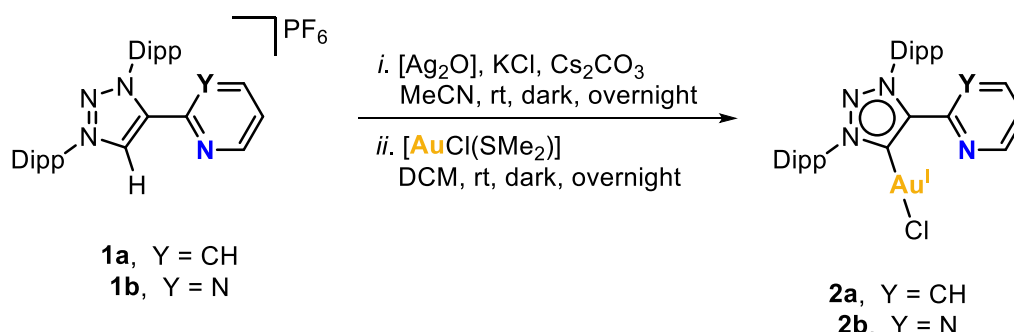
**Synthesis of 1a.** To a stirred suspension of 1,3-bis(2,6-diisopropylphenyl)triaz-1-ene (2.84 g, 7.8 mmol, 1.3 eq) and anhydrous potassium hexafluorophosphate (1.64 g, 9 mmol, 1.5 eq) in dry dichloromethane (30 mL) in the dark at -78°C was added *tert*-butyl hypochlorite (0.9 mL, 8 mmol, 1.3 eq) upon which the mixture instantly darkens. Stirring at -78°C, 2-ethynylpyridine (0.6 mL, 6 mmol, 1 eq) was added. The mixture was stirred overnight and was slowly allowed to warm to room temperature. The resulting red-brown solution was filtered using a frit funnel to remove a fine precipitate. The volatiles were then removed under reduced pressure to afford a light greenish powder, which was washed several times with diethyl ether followed by tetrahydrofuran and pentane to afford a white powder. Yield: 3.63 g (99%). <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  9.91 (s, 1H, CH<sub>trz</sub>),

8.53 (ddd,  $J = 4.8, 1.7, 0.9$  Hz, 1H,  $CH_{Ar}$ ), 7.91 (td,  $J = 7.8, 1.8$ , Hz, 1H,  $CH_{Ar}$ ), 7.77-7.70 (m, 3H,  $CH_{Ar}$ ), 7.50 (d,  $J = 7.9$  Hz, 2H,  $CH_{Ar}$ ), 7.48 (dd,  $J = 3.0, 1.1$  Hz, 1H,  $CH_{Ar}$ ), 7.45 (d,  $J = 7.9$  Hz, 2H,  $CH_{Ar}$ ), 2.38 (hept,  $J = 6.8$  Hz, 2H,  $CH(CH_3)_2$ ), 2.27 (hept,  $J = 6.8$  Hz, 2H,  $CH(CH_3)_2$ ), 1.36 (d,  $J = 6.8$  Hz, 6H,  $CH(CH_3)_2$ ), 1.21 (dd,  $J = 6.8$  Hz, 12H,  $CH(CH_3)_2$ ), 1.06 (d,  $J = 6.8$  Hz, 6H,  $CH(CH_3)_2$ ).  $^{13}C$  NMR (101 MHz,  $CD_2Cl_2$ ):  $\delta$  151.1 ( $CH_{Ar}$ ), 145.6 ( $C_{Ar}$ ), 145.6 ( $C_{Ar}$ ), 145.1 ( $C_{Ar}$ ), 141.8 ( $C_{trz}$ ), 138.7 ( $CH_{Ar}$ ), 134.1 ( $CH_{Ar}$ ), 133.7 ( $CH_{Ar}$ ), 132.3 ( $CH_{trz}$ ), 131.1 ( $C_{Ar}$ ), 131.0 ( $C_{Ar}$ ), 127.3 ( $CH_{Ar}$ ), 125.6 ( $CH_{Ar}$ ), 125.0 ( $CH_{Ar}$ ), 30.3 ( $CH(CH_3)_2$ ), 30.0 ( $CH(CH_3)_2$ ), 25.1 ( $CH(CH_3)_2$ ), 25.0 ( $CH(CH_3)_2$ ), 23.8 ( $CH(CH_3)_2$ ), 23.1 ( $CH(CH_3)_2$ ). **HRMS (ESI+)**: calculated for  $C_{31}H_{39}F_6N_4P$   $[M-PF_6]^+$ :  $m/z$  467.3175; found:  $m/z$  467.3172.

**Synthesis of 1b.** To a stirred suspension of 1,3-bis(2,6-diisopropylphenyl)triaz-1-ene (4.58 g, 9.6 mmol, 1 eq) and anhydrous potassium hexafluorophosphate (2.65 g, 14.4 mmol, 1.5 eq) in dry dichloromethane (30 mL) in the dark at  $-78^\circ C$  was added *tert*-butyl hypochlorite (1.45 mL, 12.9 mmol, 1.3 eq) upon which the mixture instantly darkens. Stirring was pursued at  $-78^\circ C$  for 30 min and 2-ethynylpyrimidine (1 g, 9.6 mmol, 1 eq) was added. The mixture was stirred overnight and was slowly allowed to warm to room temperature. The resulting dark solution was filtered using a frit funnel, and the solid residue was washed with dichloromethane. The filtrate was collected, and the volatiles were removed under reduced pressure to afford a dark green foam, which was washed several times with diethyl ether, followed by tetrahydrofuran and pentane to afford a white powder. Yield: 3.94 g (67 %).  $^1H$  NMR (400 MHz,  $CD_2Cl_2$ ):  $\delta$  9.24 (s, 1H,  $CH_{trz}$ ), 8.80 (d,  $J = 5.0$  Hz, 2H,  $CH_{pym}$ ), 7.77 (t,  $J = 7.9$  Hz, 1H,  $CH_{Ar}$ ), 7.72 (t,  $J = 7.8$  Hz, 1H,  $CH_{Ar}$ ), 7.55 – 7.49 (m, 3H: 1H  $CH_{pym}$  and 2H  $CH_{Ar}$ ), 7.44 (d,  $J = 7.9$  Hz, 2H,  $CH_{Ar}$ ), 2.37 (hept,  $J = 6.8$  Hz, 2H,  $CH(CH_3)_2$ ), 2.23 (hept,  $J = 6.7$  Hz, 2H,  $CH(CH_3)_2$ ), 1.36 (d,  $J = 6.8$  Hz, 6H,  $CH(CH_3)_2$ ), 1.21 (dd,  $J = 14.2, 6.9$  Hz, 12H,  $CH(CH_3)_2$ ), 1.06 (d,  $J = 6.8$  Hz, 6H,  $CH(CH_3)_2$ ).  $^{13}C$  NMR (101 MHz,  $CD_2Cl_2$ ):  $\delta$  158.8 ( $CH_{Ar}$ ), 152.8 ( $C_{Ar}$ ), 145.6 ( $C_{Ar}$ ), 145.3 ( $C_{Ar}$ ), 144.0 ( $C_{trz}$ ), 134.3 ( $CH_{Ar}$ ), 134.2 ( $CH_{Ar}$ ), 133.6 ( $CH_{trz}$ ), 131.3 ( $C_{Ar}$ ), 130.8 ( $C_{Ar}$ ), 125.7 ( $CH_{Ar}$ ), 125.4 ( $CH_{Ar}$ ), 123.8 ( $CH_{Ar}$ ), 30.3 ( $CH(CH_3)_2$ ), 30.1 ( $CH(CH_3)_2$ ), 25.1 ( $CH(CH_3)_2$ ), 24.9 ( $CH(CH_3)_2$ ), 23.9 ( $CH(CH_3)_2$ ), 23.2 ( $CH(CH_3)_2$ ). **HRMS (ESI+)**: calculated for  $C_{31}H_{39}F_6N_4P$   $[M-PF_6]^+$ :  $m/z$  468.3127; found:  $m/z$  468.3117.

### 3. Synthesis and reactivity of gold MIC complexes

#### 3.1 General procedure for the synthesis of gold(I) complexes **2a** and **2b**



**Scheme S2.** Synthesis of gold(I)-MIC complexes **2a** and **2b**.

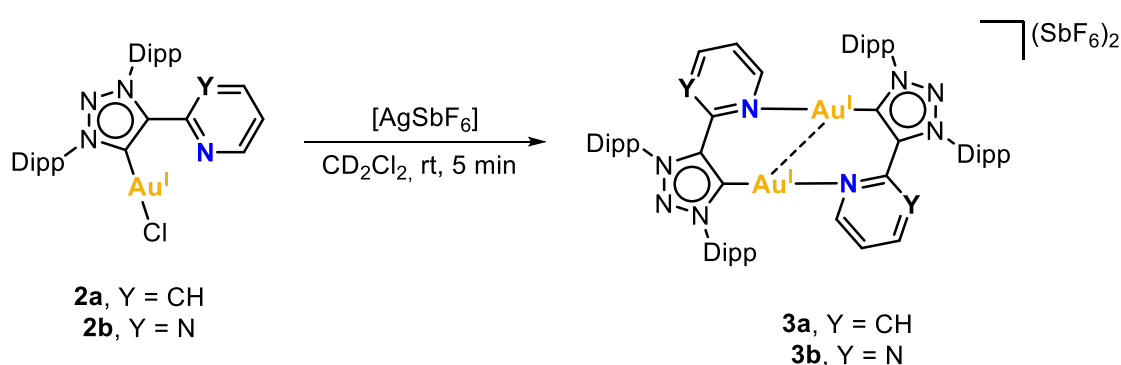
For the synthesis of Au(I) MIC complexes we followed a similar procedure to that reported in the literature.<sup>4</sup> A solution of the corresponding triazolium salt (1 eq), silver(I) oxide (1.5 eq), potassium chloride (2 eq) and cesium carbonate (3 eq) in anhydrous acetonitrile was stirred overnight at room temperature under exclusion of light. After this time, the solution was filtered over Celite® and all volatiles were removed under vacuum. The obtained residue was dissolved in anhydrous dichloromethane, followed by the addition in one portion of dimethylsulfide gold(I) chloride. The resulting reaction mixture was stirred overnight at room temperature under exclusion of light. Then, the solution was filtered over Celite®, and all the volatiles were removed under vacuum. The product was purified by chromatographic column, using silica gel as stationary phase and dichloromethane as mobile phase. After the column, the fractions that contained the product were combined, and the solvent was reduced to the minimal portion. The addition of diethyl ether affords a white-off solid that contained the desired product. The gold complexes can be further crystallized by slow diffusion of diethyl ether into a concentrated solution of the complex in dichloromethane.

**Synthesis of 2a.** For the synthesis of **2a** was employed the triazolium salt **1a** (418.2 mg, 0.68 mmol, 1.0 eq), Ag<sub>2</sub>O (256.9 mg, 1.11 mmol, 1.6 eq), KCl (121.2 mg, 1.63 mmol, 2.4 eq) and Cs<sub>2</sub>CO<sub>3</sub> (678.0 mg, 2.08 mmol, 3.0 eq) in acetonitrile (55 mL), and [AuCl(SMe<sub>2</sub>)] (197.3 mg, 0.67 mmol, 1.0 eq) in dichloromethane (55 mL). Yield: 154.7 mg (32%). <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 8.65 (dt, *J* = 8.0, 1.1 Hz, 1H, CH<sub>py</sub>), 8.30 (ddd, *J* = 4.8, 1.8, 1.0 Hz, 1H, CH<sub>py</sub>), 7.84 (td, *J* = 7.8, 1.8 Hz, 1H, CH<sub>py</sub>), 7.65 (t, *J* = 7.8 Hz, 1H, CH<sub>Ar</sub>), 7.54 (t, *J* = 7.8 Hz, 1H, CH<sub>Ar</sub>), 7.41 (d, *J* = 7.9 Hz, 2H, CH<sub>Ar</sub>), 7.29–7.26 (m, 3H: 2H CH<sub>Ar</sub> and 1H CH<sub>py</sub>), 2.51 (hept, *J* = 6.9 Hz, 2H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.36 (hept, *J* = 6.9 Hz, 2H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.41 (d, *J* = 6.8 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.19 (d, *J* = 6.9 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.14 (d, *J* = 6.9 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.01 (d, *J* = 6.8 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C NMR (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 162.1 (C<sub>carbene</sub>-Au), 149.7 (CH<sub>py</sub>), 147.3 (C<sub>trz</sub>), 146.5 (C<sub>py</sub>), 145.8 (C<sub>Ar</sub>, 2C), 145.7 (C<sub>Ar</sub>, 2C), 137.4 (CH<sub>py</sub>), 135.7 (C<sub>Ar</sub>), 132.9 (C<sub>Ar</sub>), 132.2 (CH<sub>Ar</sub>),

131.9 ( $\text{CH}_{\text{Ar}}$ ), 125.0 ( $\text{CH}_{\text{py}}$ ), 125.0 ( $\text{CH}_{\text{Ar}}$ , 2C), 124.9 ( $\text{CH}_{\text{py}}$ ), 124.4 ( $\text{CH}_{\text{Ar}}$ , 2C), 30.0 ( $\text{CH}(\text{CH}_3)_2$ ), 29.6 ( $\text{CH}(\text{CH}_3)_2$ ), 25.1 ( $\text{CH}(\text{CH}_3)_2$ ), 24.7 ( $\text{CH}(\text{CH}_3)_2$ ), 24.5 ( $\text{CH}(\text{CH}_3)_2$ ), 23.0 ( $\text{CH}(\text{CH}_3)_2$ ). **HRMS (ESI+)**: calcd for  $\text{C}_{31}\text{H}_{38}\text{N}_4\text{AuCl}$  [ $\text{M}+\text{Na}$ ] $^+$ :  $m/z$  721.2343; found:  $m/z$  721.2322.

**Synthesis of 2b.** For the synthesis of **2b** was employed the azolium salt **1b** (499.7 mg, 0.81 mmol, 1.0 eq),  $\text{Ag}_2\text{O}$  (290.5 mg, 1.25 mmol, 1.5 eq), KCl (126.1 mg, 1.69 mmol, 2.1 eq) and  $\text{Cs}_2\text{CO}_3$  (808.6 mg, 2.48 mmol, 3.0 eq) in acetonitrile (65 mL), and  $[\text{AuCl}(\text{SMe}_2)]$  (243.6 mg, 0.83 mmol, 1.0 eq) in dichloromethane (65 mL). Yield: 199.7 mg (35%).  **$^1\text{H}$  NMR** (400 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  8.71 (d,  $J = 4.9$  Hz, 2H,  $\text{CH}_{\text{pym}}$ ), 7.65 (t,  $J = 7.8$  Hz, 1H,  $\text{CH}_{\text{Ar}}$ ), 7.56 (t,  $J = 7.8$  Hz, 1H,  $\text{CH}_{\text{Ar}}$ ), 7.41 (d,  $J = 7.8$  Hz, 2H,  $\text{CH}_{\text{Ar}}$ ), 7.32 – 7.28 (m, 3H: 2H  $\text{CH}_{\text{Ar}}$  and 1H  $\text{CH}_{\text{pym}}$ ), 2.52 (hept,  $J = 6.8$  Hz, 2H,  $\text{CH}(\text{CH}_3)_2$ ), 2.37 (hept,  $J = 6.8$  Hz, 2H,  $\text{CH}(\text{CH}_3)_2$ ), 1.41 (d,  $J = 6.8$  Hz, 6H,  $\text{CH}(\text{CH}_3)_2$ ), 1.19 (d,  $J = 6.9$  Hz, 6H,  $\text{CH}(\text{CH}_3)_2$ ), 1.15 (d,  $J = 6.9$  Hz, 6H,  $\text{CH}(\text{CH}_3)_2$ ), 1.02 (d,  $J = 6.8$  Hz, 6H,  $\text{CH}(\text{CH}_3)_2$ ).  **$^{13}\text{C}$  NMR** (101 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  165.3 ( $\text{C}_{\text{carbene-Au}}$ ), 157.8 ( $\text{CH}_{\text{pym}}$ , 2C), 156.5 ( $\text{C}_{\text{pym}}$ ), 146.5 ( $\text{C}_{\text{trz}}$ ), 145.8 ( $\text{C}_{\text{Ar}}$ , 2C), 145.7 ( $\text{C}_{\text{Ar}}$ , 2C), 135.7 ( $\text{C}_{\text{Ar}}$ ), 132.7 ( $\text{C}_{\text{Ar}}$ ), 132.3 ( $\text{CH}_{\text{Ar}}$ ), 132.1 ( $\text{CH}_{\text{Ar}}$ ), 125.0 ( $\text{CH}_{\text{Ar}}$ , 2C), 124.6 ( $\text{CH}_{\text{Ar}}$ , 2C), 121.5 ( $\text{CH}_{\text{pym}}$ ), 29.9 ( $\text{CH}(\text{CH}_3)_2$ ), 29.6 ( $\text{CH}(\text{CH}_3)_2$ ), 25.1 ( $\text{CH}(\text{CH}_3)_2$ ), 24.7 ( $\text{CH}(\text{CH}_3)_2$ ), 24.4 ( $\text{CH}(\text{CH}_3)_2$ ), 23.2 ( $\text{CH}(\text{CH}_3)_2$ ). **HRMS (ESI+)**: calcd for  $\text{C}_{30}\text{H}_{37}\text{N}_5\text{AuCl}$  [ $\text{M}+\text{Na}$ ] $^+$ :  $m/z$  722.2295; found:  $m/z$  722.2273.

### 3.2 General procedure for the synthesis of dimeric gold(I) complexes **3a** and **3b**



**Scheme S3.** Synthesis of dimeric gold(I)-MIC complexes **3a** and **3b**.

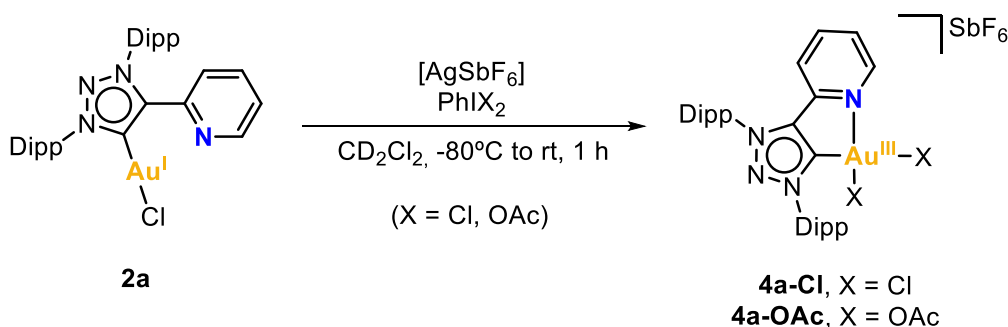
This procedure was carried out under nitrogen atmosphere using glovebox techniques. To a solution of  $[\text{AgSbF}_6]$  in  $\text{CD}_2\text{Cl}_2$  (0.2 mL) was added a solution of **2a** or **2b** in  $\text{CD}_2\text{Cl}_2$  (0.5 mL). The resulting reaction mixture was stirred at room temperature for 5 min, then filtered through a micro filter and evaporated under vacuum. The resulting dimeric gold(I) complexes were obtained as white solids. For the case of **3a**, diethyl ether was slowly

diffused into a solution of the complex in dichloromethane, obtaining crystals that were suitable for X-ray diffraction.

**Synthesis of 3a.** 14.6 mg of **2a** (0.02 mmol, 1.0 eq) were mixed with 7.2 mg of [AgSbF<sub>6</sub>] (0.02 mmol, 1.0 eq). Yield: 17.5 mg (93%). <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 8.65 (dd, *J* = 5.7, 1.6 Hz, 2H, CH<sub>py</sub>), 7.94 (td, *J* = 8.0, 1.7 Hz, 2H, CH<sub>py</sub>), 7.75 – 7.66 (m, 6H: 2H CH<sub>py</sub> and 4H CH<sub>Ar</sub>), 7.49 (d, *J* = 7.9 Hz, 4H, CH<sub>Ar</sub>), 7.41 (d, *J* = 7.9 Hz, 4H, CH<sub>Ar</sub>), 7.31 (dd, *J* = 8.3, 1.3 Hz, 2H, CH<sub>py</sub>), 2.42 (hept, *J* = 6.8 Hz, 4H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.25 (br s, 4H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.45 (d, *J* = 6.7 Hz, 12H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.26 (d, *J* = 6.8 Hz, 12H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.16 (d, *J* = 6.8 Hz, 12H, CH(CH<sub>3</sub>)<sub>2</sub>), 0.95 (br s, 12H, CH(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C NMR (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 157.2 (C<sub>carbene-Au</sub>), 154.5 (CH<sub>py</sub>), 147.0 (C<sub>trz</sub>), 145.5 – 145.2 (C<sub>Ar</sub> and C<sub>py</sub>), 141.7 (CH<sub>py</sub>), 135.0 (C<sub>Ar</sub>), 134.3 (CH<sub>Ar</sub>), 133.4 (CH<sub>Ar</sub>), 130.4 (CH<sub>py</sub>), 130.1 (C<sub>Ar</sub>), 128.7 (CH<sub>py</sub>), 126.4 (CH<sub>Ar</sub>), 125.5 (CH<sub>Ar</sub>), 30.1 (CH(CH<sub>3</sub>)<sub>2</sub>), 30.0 (CH(CH<sub>3</sub>)<sub>2</sub>), 26.0 (CH(CH<sub>3</sub>)<sub>2</sub>), 24.9 (CH(CH<sub>3</sub>)<sub>2</sub>), 24.7 (CH(CH<sub>3</sub>)<sub>2</sub>), 22.7 (CH(CH<sub>3</sub>)<sub>2</sub>). **HRMS (ESI+):** calcd for C<sub>31</sub>H<sub>38</sub>AuN<sub>4</sub> [(MIC<sup>N<sup>py</sup></sup>)Au+MeCN]<sup>+</sup>: *m/z* 704.3027; found: *m/z* 704.3025.

**Synthesis of 3b.** 14.8 mg of **2b** (0.02 mmol, 1.0 eq) were mixed with 8.0 mg of [AgSbF<sub>6</sub>] (0.02 mmol, 1.1 eq). Yield: 18.9 mg (99%). <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 8.83 (dd, *J* = 5.8, 2.2 Hz, 2H, CH<sub>pym</sub>), 8.73 (dd, *J* = 4.8, 2.2 Hz, 2H, CH<sub>pym</sub>), 7.73 – 7.67 (m, 4H: 2H CH<sub>Ar</sub> and 2H CH<sub>pym</sub>), 7.62 (t, *J* = 7.9 Hz, 2H, CH<sub>Ar</sub>), 7.47 (d, *J* = 7.9 Hz, 4H, CH<sub>Ar</sub>), 7.35 (d, *J* = 7.9 Hz, 4H, CH<sub>Ar</sub>), 2.39 (hept, *J* = 6.6 Hz, 4H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.26 – 2.15 (m, 4H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.43 (d, *J* = 6.8 Hz, 12H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.26 (d, *J* = 6.8 Hz, 12H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.16 (d, *J* = 6.8 Hz, 12H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.01 (d, *J* = 6.7 Hz, 12H, CH(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C NMR (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 161.3 (CH<sub>pym</sub>), 160.4 (CH<sub>pym</sub>), 157.2 (C<sub>carbene-Au</sub>), 154.8 (C<sub>pym</sub>), 145.8 (C<sub>trz</sub>), 145.5 (br s, C<sub>Ar</sub>), 134.8 (C<sub>Ar</sub>), 133.5 (CH<sub>Ar</sub>), 133.3 (CH<sub>Ar</sub>), 131.7 (C<sub>Ar</sub>), 125.6 (CH<sub>Ar</sub>), 125.2 (CH<sub>Ar</sub>), 123.9 (CH<sub>pym</sub>), 30.4 (CH(CH<sub>3</sub>)<sub>2</sub>), 29.9 (CH(CH<sub>3</sub>)<sub>2</sub>), 25.3 (CH(CH<sub>3</sub>)<sub>2</sub>), 25.1 (CH(CH<sub>3</sub>)<sub>2</sub>), 24.6 (CH(CH<sub>3</sub>)<sub>2</sub>), 23.2 (CH(CH<sub>3</sub>)<sub>2</sub>). **HRMS (ESI+):** calcd for C<sub>30</sub>H<sub>37</sub>AuN<sub>5</sub> [(MIC<sup>N<sup>pym</sup></sup>)Au+MeCN]<sup>+</sup>: *m/z* 705.2980; found: *m/z* 705.2991.

### 3.3 General procedure for the synthesis of gold(III) complexes **4a-Cl** and **4a-OAc** via oxidation



**Scheme S4.** Synthesis of gold(III)-MIC complexes **4a-Cl** and **4a-OAc**.

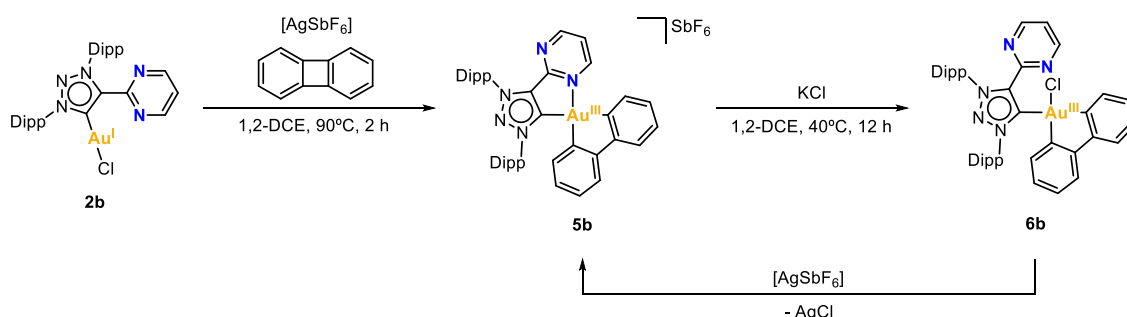
Under nitrogen atmosphere, a vial was charged with **2a** in  $\text{CD}_2\text{Cl}_2$  (0.15 mL) and cooled to  $-80^\circ\text{C}$ . Afterwards,  $[\text{AgSbF}_6]$  in  $\text{CD}_2\text{Cl}_2$  (0.3 mL) and  $\text{PhICl}_2$  or  $\text{PhI}(\text{OAc})_2$  in  $\text{CD}_2\text{Cl}_2$  (0.3 mL) were added. The  $\text{PhICl}_2$  used was freshly prepared following a reported procedure.<sup>5</sup> Then, the reaction mixture was stirred and slowly warmed up to room temperature. During this time, an intense yellow color was observed with the concomitant formation of a grey solid. After 1h at room temperature, the reaction mixture was filtered over Celite®, obtaining a yellow solution. The  $^1\text{H}$  NMR of the reaction mixture revealed that complex **2a** was quantitatively consumed. Slow diffusion of diethyl ether into this latter solution afforded crystals of the desired product.

**Synthesis of 4a-Cl.** 20.1 mg of **2a** (0.03 mmol, 1.0 eq) were mixed with 11.4 mg of  $\text{AgSbF}_6$  (0.03 mmol, 1.2 eq) and 9.2 mg of  $\text{PhICl}_2$  (0.03 mmol, 1.2 eq). **4a-Cl** was obtained as pale-yellow needles. Yield: 19.6 mg (70%).  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  9.83 (dd,  $J = 6.0, 1.4$  Hz, 1H,  $\text{CH}_{\text{py}}$ ), 8.27 (td,  $J = 7.9, 1.4$  Hz, 1H,  $\text{CH}_{\text{py}}$ ), 7.96 (ddd,  $J = 7.7, 6.0, 1.5$  Hz, 1H,  $\text{CH}_{\text{py}}$ ), 7.89 (t,  $J = 7.9$  Hz, 1H,  $\text{CH}_{\text{Ar}}$ ), 7.72 (t,  $J = 7.9$  Hz, 1H,  $\text{CH}_{\text{Ar}}$ ), 7.62 (d,  $J = 7.9$  Hz, 2H,  $\text{CH}_{\text{Ar}}$ ), 7.44 (d,  $J = 7.9$  Hz, 2H,  $\text{CH}_{\text{Ar}}$ ), 6.83 (ddd,  $J = 8.0, 1.6, 0.6$  Hz, 1H,  $\text{CH}_{\text{py}}$ ), 2.40 – 2.25 (m, 4H,  $\text{CH}(\text{CH}_3)_2$ ), 1.36 (d,  $J = 6.7$  Hz, 6H,  $\text{CH}(\text{CH}_3)_2$ ), 1.21 – 1.17 (m, 18H,  $\text{CH}(\text{CH}_3)_2$ ).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  152.0 ( $\text{CH}_{\text{py}}$ ), 149.0 ( $\text{C}_{\text{trz}}$ ), 147.3 ( $\text{C}_{\text{carbene-Au}}$ ), 145.9 ( $\text{C}_{\text{Ar}}$ ), 145.9 ( $\text{CH}_{\text{py}}$ ), 145.7 ( $\text{C}_{\text{Ar}}$ ), 143.7 ( $\text{C}_{\text{py}}$ ), 135.3 ( $\text{CH}_{\text{Ar}}$ ), 133.7 ( $\text{CH}_{\text{Ar}}$ ), 132.1 ( $\text{C}_{\text{Ar}}$ ), 130.1 ( $\text{CH}_{\text{py}}$ ), 128.6 ( $\text{C}_{\text{Ar}}$ ), 126.8 ( $\text{CH}_{\text{Ar}}$ ), 125.1 ( $\text{CH}_{\text{Ar}}$ ), 123.8 ( $\text{CH}_{\text{py}}$ ), 30.2 ( $\text{CH}(\text{CH}_3)_2$ ), 30.1 ( $\text{CH}(\text{CH}_3)_2$ ), 25.6 ( $\text{CH}(\text{CH}_3)_2$ ), 25.3 ( $\text{CH}(\text{CH}_3)_2$ ), 23.4 ( $\text{CH}(\text{CH}_3)_2$ ), 23.4 ( $\text{CH}(\text{CH}_3)_2$ ). **HRMS (ESI+)**: calcd for  $\text{C}_{31}\text{H}_{38}\text{AuCl}_2\text{F}_6\text{N}_4\text{Sb}$   $[\text{M-SbF}_6]^+$ :  $m/z$  733.2134; found:  $m/z$  733.2132.



**Synthesis of 4a-OAc.** 20.0 mg of **2a** (0.03 mmol, 1.0 eq) were mixed with 11.8 mg of AgSbF<sub>6</sub> (0.03 mmol, 1.2 eq) and 10.9 mg of PhI(OAc)<sub>2</sub> (0.03 mmol, 1.2 eq). **4a-OAc** was obtained as yellow blocks. Yield: 27.5 mg (95%). <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 8.88 (dd, *J* = 5.9, 1.4 Hz, 1H, CH<sub>py</sub>), 8.30 (td, *J* = 7.9, 1.4 Hz, 1H, CH<sub>py</sub>), 7.95 – 7.87 (m, 2H: 1H CH<sub>py</sub> and 1H CH<sub>Ar</sub>), 7.71 (t, *J* = 7.8 Hz, 1H, CH<sub>Ar</sub>), 7.62 (d, *J* = 7.9 Hz, 2H, CH<sub>Ar</sub>), 7.48 (d, *J* = 7.9 Hz, 2H, CH<sub>Ar</sub>), 6.82 (dd, *J* = 8.0, 1.4 Hz, 1H, CH<sub>py</sub>), 2.45 (hept, *J* = 6.9 Hz, 2H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.26 (hept, *J* = 6.8 Hz, 2H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.14 (s, 3H, CH<sub>3</sub>COO *cis* to py), 1.45 (d, *J* = 6.7 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.36 (s, 3H, CH<sub>3</sub>COO *trans* to py), 1.21 – 1.15 (m, 18H, CH(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C NMR (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 176.7 (COOCH<sub>3</sub> *cis* to py), 174.9 (COOCH<sub>3</sub> *trans* to py), 151.8 (CH<sub>py</sub>), 148.5 (C<sub>trz</sub>), 146.3 (CH<sub>py</sub>), 146.3 (C<sub>Ar</sub>), 145.8 (C<sub>Ar</sub>), 143.9 (C<sub>py</sub>), 137.1 (C<sub>carbene-Au</sub>), 135.4 (CH<sub>Ar</sub>), 133.9 (CH<sub>Ar</sub>), 131.3 (C<sub>Ar</sub>), 129.9 (CH<sub>py</sub>), 128.3 (C<sub>Ar</sub>), 126.9 (CH<sub>Ar</sub>), 125.4 (CH<sub>Ar</sub>), 123.6 (CH<sub>py</sub>), 30.3 (CH(CH<sub>3</sub>)<sub>2</sub>), 30.0 (CH(CH<sub>3</sub>)<sub>2</sub>), 26.2 (CH(CH<sub>3</sub>)<sub>2</sub>), 25.5 (CH(CH<sub>3</sub>)<sub>2</sub>), 23.7 (CH(CH<sub>3</sub>)<sub>2</sub>), 23.2 (COOCH<sub>3</sub> *cis* to py), 22.6 (CH(CH<sub>3</sub>)<sub>2</sub>), 19.0 (COOCH<sub>3</sub> *trans* to py). HRMS (ESI<sup>+</sup>): calcd for C<sub>35</sub>H<sub>44</sub>AuF<sub>6</sub>N<sub>4</sub>O<sub>4</sub>Sb [M-SbF<sub>6</sub>]<sup>+</sup>: *m/z* 781.3023; found: *m/z* 781.3022.

### 3.4 Synthesis of gold(III) complexes **5b** and **6b** via oxidative addition



**Scheme S5.** Synthesis of gold(III)-MIC complexes **5b** and **6b**.

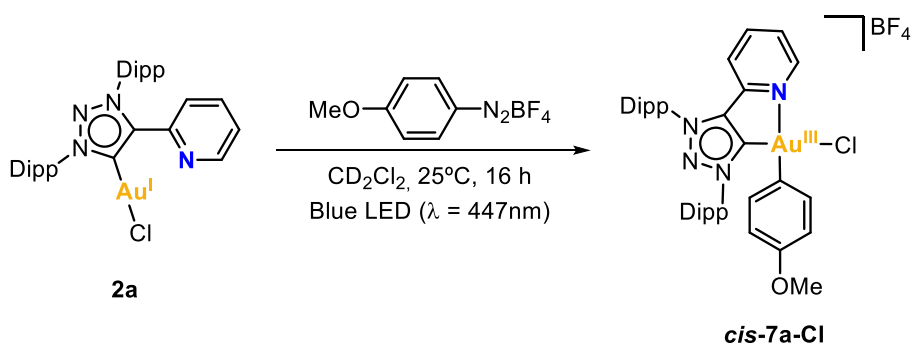
Under nitrogen atmosphere, a solution of **2b** (10.6 mg, 0.02 mmol, 1 eq) and biphenylene (10.4 mg, 0.07 mmol, 4.5 eq) in 1,2-dichloroethane (0.4 mL) was added to a solution of [AgSbF<sub>6</sub>] (7.0 mg, 0.02 mmol, 1.3 eq) in 1,2-dichloroethane (0.35 mL). The reaction mixture was then stirred and heated at 90°C for 2h. After this time, it was filtered through a micro filter, obtaining a green solution that contains **5b**. Then, powdered KCl (12.1 mg, 0.16 mmol, 10.7 eq) was added and the mixture was stirred for 12h at 40°C. After the solution was cooled down to room temperature, it was filtered through a micro-filter to obtain a clear yellow solution. All the volatiles were removed under vacuum, and the solid residue was dissolved in the minimal amount of dichloromethane. By slow diffusion of diethyl ether into this latter solution, crystals of the desired complex **6b** were obtained.

For the synthesis of **5b**, [AgSbF<sub>6</sub>] (6.2 mg, 0.02 mmol, 1.5 eq) was added to a solution of **6b** (10.4 mg, 0.01 mmol, 1 eq) in dichloromethane (0.5 mL) and the mixture was stirred at room temperature for 10 minutes. Then, it was filtered through a micro filter to obtain a clear yellow solution. The volatiles were removed under vacuum, yielding the desired complex **5b** as a pale yellow solid.

**Synthesis of 6b.** Yield: 7.7 mg (60%). <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 8.56 (d, *J* = 4.9 Hz, 2H, CH<sub>pym</sub>), 8.02 (dd, *J* = 7.5, 1.4 Hz, 1H, CH<sub>BPL</sub>), 7.62 (t, *J* = 7.8 Hz, 1H, CH<sub>Ar</sub>), 7.55 (t, *J* = 7.8 Hz, 1H, CH<sub>Ar</sub>), 7.43 (dd, *J* = 7.8, 1.4 Hz, 1H, CH<sub>Ar</sub>), 7.39 (dd, *J* = 7.8, 1.4 Hz, 1H, CH<sub>Ar</sub>), 7.32 (dd, *J* = 7.8, 1.4 Hz, 1H, CH<sub>Ar</sub>), 7.29 (dd, *J* = 7.7, 1.5 Hz, 2H, CH<sub>BPL</sub>), 7.24 (dd, *J* = 7.8, 1.4 Hz, 1H, CH<sub>Ar</sub>), 7.12 (t, *J* = 4.9 Hz, 1H, CH<sub>pym</sub>), 7.08 (td, *J* = 7.4, 1.4 Hz, 1H, CH<sub>BPL</sub>), 7.00 (tdd, *J* = 7.4, 5.9, 1.4 Hz, 2H, CH<sub>BPL</sub>), 6.81 (dd, *J* = 7.7, 1.2 Hz, 1H, CH<sub>BPL</sub>), 6.58 (td, *J* = 7.6, 1.5 Hz, 1H, CH<sub>BPL</sub>), 2.83 – 2.69 (m, 2H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.53 – 2.42 (m, 2H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.50 (d, *J* = 6.6 Hz, 3H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.34 (d, *J* = 6.8 Hz, 3H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.27 (d, *J* = 6.8 Hz, 3H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.21 (d, *J* = 6.8 Hz, 3H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.16 (d, *J* = 6.9 Hz, 3H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.01 (d, *J* = 6.9 Hz, 3H, CH(CH<sub>3</sub>)<sub>2</sub>), 0.79 (d, *J* = 6.8 Hz, 3H, CH(CH<sub>3</sub>)<sub>2</sub>), 0.71 (d, *J* = 6.7 Hz, 3H, CH(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C NMR (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 180.1 (C<sub>carbene-Au</sub>), 160.3 (C<sub>BPL-Au trans to carbene</sub>), 157.7 (CH<sub>pym</sub>, 2C), 156.6 (C<sub>pym</sub>), 154.9 (C<sub>BPL</sub>), 153.7 (C<sub>BPL</sub>), 152.3 (C<sub>BPL-Au cis to carbene</sub>), 147.4 (C<sub>Ar</sub>), 146.4 (C<sub>Ar</sub>), 146.2 (C<sub>trz</sub>), 145.4 (C<sub>Ar</sub>), 145.1 (C<sub>Ar</sub>), 134.9 (C<sub>Ar</sub>), 133.5 (CH<sub>BPL</sub>), 132.6 (C<sub>Ar</sub>), 132.2 (CH<sub>Ar</sub>), 132.1 (CH<sub>Ar</sub>), 131.8 (CH<sub>BPL</sub>), 127.3 (CH<sub>BPL</sub>), 127.1 (CH<sub>BPL</sub>), 126.9 (CH<sub>BPL</sub>), 126.6 (CH<sub>BPL</sub>), 124.8 (CH<sub>Ar</sub>, 3C), 124.6 (CH<sub>Ar</sub>), 121.8 (CH<sub>BPL</sub>), 121.3 (CH<sub>pym</sub>), 120.8 (CH<sub>BPL</sub>), 30.4 (CH(CH<sub>3</sub>)<sub>2</sub>), 30.3 (CH(CH<sub>3</sub>)<sub>2</sub>), 29.6 (CH(CH<sub>3</sub>)<sub>2</sub>), 29.5 (CH(CH<sub>3</sub>)<sub>2</sub>), 27.4 (CH(CH<sub>3</sub>)<sub>2</sub>), 26.0 (CH(CH<sub>3</sub>)<sub>2</sub>), 25.0 (CH(CH<sub>3</sub>)<sub>2</sub>), 24.8 (CH(CH<sub>3</sub>)<sub>2</sub>), 23.7 (CH(CH<sub>3</sub>)<sub>2</sub>), 23.5 (CH(CH<sub>3</sub>)<sub>2</sub>), 23.0 (CH(CH<sub>3</sub>)<sub>2</sub>), 22.2 (CH(CH<sub>3</sub>)<sub>2</sub>). **HRMS (ESI+):** calcd for C<sub>42</sub>H<sub>45</sub>AuClN<sub>5</sub> [M-Cl]<sup>+</sup>: *m/z* 816.3335; found: *m/z* 816.3342.

**Synthesis of 5b.** Yield: 12.2 mg (78%). <sup>1</sup>H NMR (400 MHz, 248K, CD<sub>2</sub>Cl<sub>2</sub>) δ 9.48 (br s, 1H, CH<sub>pym</sub>), 8.98 (br s, 1H, CH<sub>pym</sub>), 7.94 (t, *J* = 5.3 Hz, 1H, CH<sub>pym</sub>), 7.75 (dt, *J* = 12.7 Hz, 7.9 Hz, 2H, CH<sub>Ar</sub>), 7.48 (d, *J* = 7.9 Hz, 4H, CH<sub>Ar</sub>), 7.41 (dd, *J* = 7.6, 1.5 Hz, 1H, CH<sub>BPL</sub>), 7.35 (d, *J* = 7.6 Hz, 1H, CH<sub>BPL</sub>), 7.32 – 7.25 (m, 2H, CH<sub>BPL</sub>), 7.20 (td, *J* = 7.5, 1.5 Hz, 1H, CH<sub>BPL</sub>), 7.04 (t, *J* = 7.3 Hz, 1H, CH<sub>BPL</sub>), 6.16 (td, *J* = 7.6, 1.6 Hz, 1H, CH<sub>BPL</sub>), 6.11 (d, *J* = 7.9 Hz, 1H, CH<sub>BPL</sub>), 2.42 (hept, *J* = 6.8 Hz, 2H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.21 (hept, *J* = 6.8 Hz, 2H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.16 (d, *J* = 6.9 Hz, 12H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.12 (d, *J* = 6.7 Hz, 12H, CH(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C NMR (101 MHz, 248K, CD<sub>2</sub>Cl<sub>2</sub>) δ 182.8 (C<sub>carbene-Au</sub>), 161.6 (CH<sub>pym</sub>), 160.1 (C<sub>BPL-Au trans to carbene</sub>), 157.7 (CH<sub>pym</sub>), 156.4 (C<sub>pym</sub>), 153.2 (C<sub>BPL</sub>), 153.2 (C<sub>BPL</sub>), 149.8 (C<sub>trz</sub>), 149.4 (C<sub>BPL-Au cis to carbene</sub>), 145.4 (C<sub>Ar</sub>, 2C), 144.9 (C<sub>Ar</sub>, 2C), 134.7 (CH<sub>BPL</sub>), 133.4 (CH<sub>Ar</sub>), 133.1 (CH<sub>Ar</sub>), 132.9 (C<sub>Ar</sub>), 131.5 (CH<sub>BPL</sub>), 130.1 (C<sub>Ar</sub>), 129.3 (CH<sub>BPL</sub>), 128.8 (CH<sub>BPL</sub>), 128.2 (CH<sub>BPL</sub>), 127.1 (CH<sub>BPL</sub>), 125.6 (CH<sub>Ar</sub>, 2C), 125.1 (CH<sub>Ar</sub>, 2C), 124.1 (CH<sub>pym</sub>), 122.6 (CH<sub>BPL</sub>), 122.5 (CH<sub>BPL</sub>), 29.8 (CH(CH<sub>3</sub>)<sub>2</sub>, 2C), 29.5 (CH(CH<sub>3</sub>)<sub>2</sub>, 2C), 25.0 (CH(CH<sub>3</sub>)<sub>2</sub>, 2C), 24.9 (CH(CH<sub>3</sub>)<sub>2</sub>, 2C), 23.2 (CH(CH<sub>3</sub>)<sub>2</sub>, 4C). **HRMS (ESI+):** calcd for C<sub>42</sub>H<sub>45</sub>AuF<sub>6</sub>N<sub>5</sub>Sb [M-SbF<sub>6</sub>]<sup>+</sup>: *m/z* 816.3335; found: *m/z* 816.3354.

### 3.5 Synthesis of gold(III) complex *cis-7a-Cl* via oxidative addition

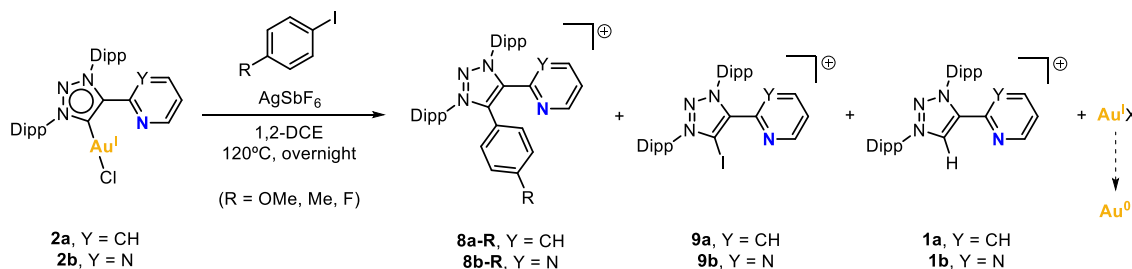


**Scheme S6.** Synthesis of gold(III)-MIC complex *cis-7a-Cl*.

The synthesis of complex *cis-7a-Cl* was carried out following a previous report that described the synthesis of Au(III) complexes by oxidative addition of diazonium salts.<sup>6</sup> Under nitrogen atmosphere, a vial was charged with **2a** (41.2 mg, 0.06 mmol, 1 eq), 4-methoxybenzenediazonium tetrafluoroborate (13.3 mg, 0.06 mmol, 1 eq) and six small glass balls. Then, CD<sub>2</sub>Cl<sub>2</sub> was added (1.8 mL) and the vial was sealed. The reaction mixture was irradiated with blue LED (λ = 447 nm) and stirred at 25°C for 16h. The <sup>1</sup>H NMR of the reaction crude showed the formation of the desired Au(III) complex in 51% yield. The desired product precipitated after the addition of cold Et<sub>2</sub>O to the reaction crude. A further recrystallization of the product was performed by slow diffusion of diethyl ether into a concentrated solution in dichloromethane. Suitable crystals for X-ray diffraction analysis were obtained from a concentrated DMF solution. Complex *cis-7a-Cl* was isolated as pale-yellow crystals. Yield: 11.7 mg (22%).

<sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 9.52 (ddd, *J* = 5.5, 1.6, 0.8 Hz, 1H, CH<sub>py</sub>), 8.19 (td, *J* = 7.9, 1.6 Hz, 1H, CH<sub>py</sub>), 7.97 (ddd, *J* = 7.9, 5.5, 1.3 Hz, 1H, CH<sub>py</sub>), 7.89 (t, *J* = 7.9 Hz, 1H, CH<sub>Ar</sub>), 7.62 (d, *J* = 7.9 Hz, 2H, CH<sub>Ar</sub>), 7.39 (t, *J* = 7.9 Hz, 1H, CH<sub>Ar</sub>), 7.10 (d, *J* = 7.9 Hz, 2H, CH<sub>Ar</sub>), 6.89 – 6.85 (m, 2H, CH<sub>Ar</sub>), 6.73 (dt, *J* = 8.0, 1.1 Hz, 1H, CH<sub>py</sub>), 6.41 – 6.36 (m, 2H, CH<sub>Ar</sub>), 3.70 (s, 3H, OCH<sub>3</sub>), 2.44 (hept, *J* = 6.8 Hz, 2H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.30 (hept, *J* = 6.8 Hz, 2H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.35 (d, *J* = 6.7 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.22 (d, *J* = 6.8 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.12 (d, *J* = 6.8 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.04 (d, *J* = 6.8 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C NMR (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 159.0 (COCH<sub>3</sub>), 151.5 (C<sub>carbene</sub>-Au), 151.3 (C<sub>trz</sub>), 150.4 (CH<sub>py</sub>), 145.8 (C<sub>Ar</sub>, 2C), 144.7 (C<sub>Ar</sub>, 2C), 144.1 (CH<sub>py</sub>), 144.0 (C<sub>py</sub>), 135.1 (CH<sub>Ar</sub>), 133.2 (CH<sub>Ar</sub>), 132.9 (C<sub>Ar</sub>), 132.5 (CH<sub>Ar</sub>, 2C), 129.7 (CH<sub>py</sub>), 128.9 (C<sub>Ar</sub>), 126.9 (CH<sub>Ar</sub>, 2C), 124.9 (CH<sub>Ar</sub>, 2C), 122.5 (CH<sub>py</sub>), 117.6 (C<sub>Ar</sub>-Au), 115.6 (CH<sub>Ar</sub>, 2C), 55.9 (OCH<sub>3</sub>), 29.8 (CH(CH<sub>3</sub>)<sub>2</sub>, 4C), 26.7 (CH(CH<sub>3</sub>)<sub>2</sub>, 2C), 25.2 (CH(CH<sub>3</sub>)<sub>2</sub>, 2C), 24.1 (CH(CH<sub>3</sub>)<sub>2</sub>, 2C), 22.0 (CH(CH<sub>3</sub>)<sub>2</sub>, 2C). HRMS (ESI<sup>+</sup>): calcd for C<sub>38</sub>H<sub>45</sub>AuBClF<sub>4</sub>N<sub>4</sub>O [M-BF<sub>4</sub>]<sup>+</sup>: *m/z* 805.2942; found: *m/z* 805.2956.

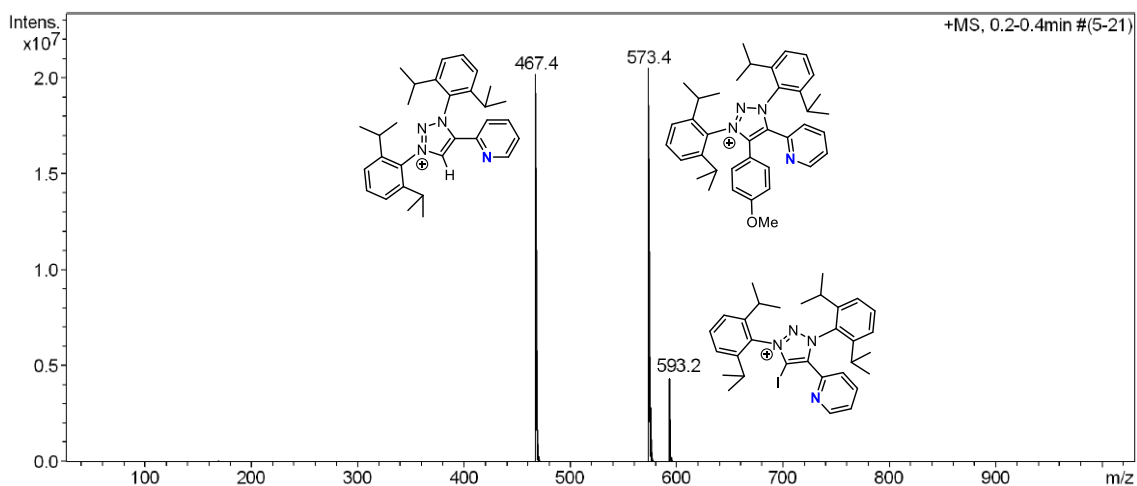
### 3.6 General procedure for the reactivity of gold(I) complexes **2a** and **2b** towards aryl halides



**Scheme S7.** Reactivity of complexes **2a** and **2b** towards aryl iodides.

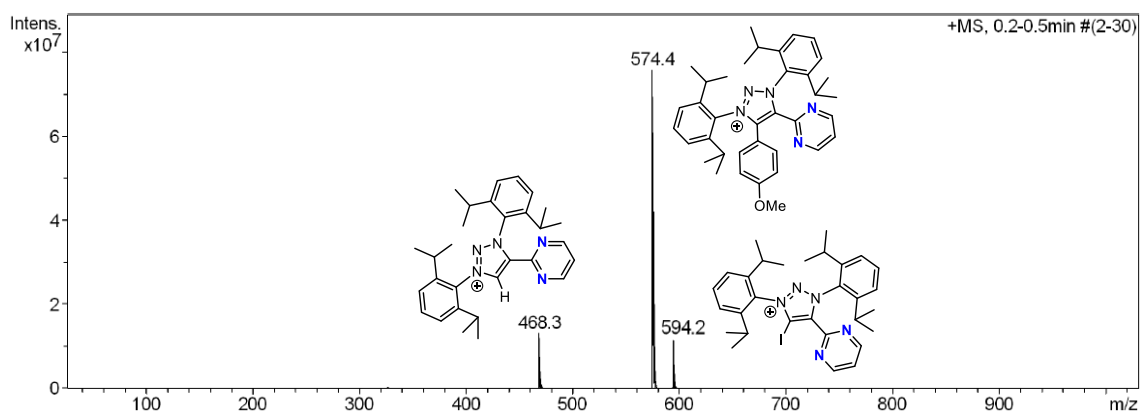
A vial was charged with **2a** or **2b** (0.015 mmol), the aryl iodide (0.06 – 0.08 mmol), a magnetic stirring bar and 1,2-dichloroethane (0.5 mL). Then,  $[\text{AgSbF}_6]$  (0.018 mmol) was added to the reaction mixture. The vial was sealed, stirred, and heated at  $120^\circ\text{C}$  overnight in the absence of light. After this time, the brown suspension was filtered, and all the volatiles were removed under vacuum. Then,  $\text{CD}_2\text{Cl}_2$  was added to analyze the reaction outcome by  $^1\text{H}$  NMR. By adding 1,3,5-trimethoxybenzene as internal standard, the yields of the products could be determined.

**Reactivity of 2a with 4-iodoanisole.** Complex **2a** (11.6 mg, 0.017 mmol, 1 eq),  $[\text{AgSbF}_6]$  (7.1 mg, 0.021 mmol, 1.25 eq) and 4-iodoanisole (21.0 mg, 0.090 mmol, 5.4 eq) were employed. NMR yield: 41% (**8a-OMe**), 3% (**9a**), 24% (**1a**). Suitable crystals for X-ray diffraction analysis were obtained by slow diffusion of diethyl ether into a concentrated solution of the filtered crude in dichloromethane, showing the co-crystallization of **8a-OMe** and **9a** in a 0.89:0.11 ratio, respectively (see Figure S98).



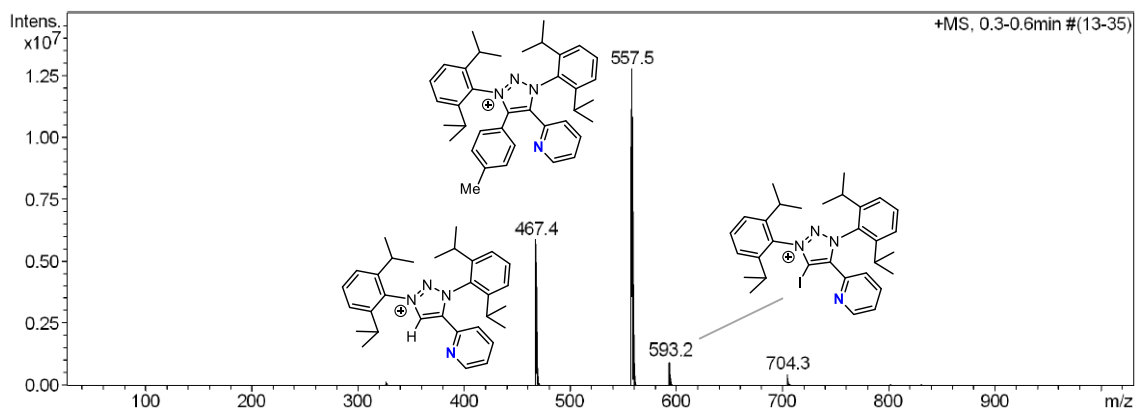
**Figure S1.** MS-ESI(+) of the reaction crude showing the peaks of **1a**, **8a-OMe** and **9a**.

**Reactivity of 2b with 4-iodoanisole.** Complex **2b** (10.0 mg, 0.014 mmol, 1 eq), [AgSbF<sub>6</sub>] (5.3 mg, 0.015 mmol, 1.08 eq) and 4-iodoanisole (15.6 mg, 0.067 mmol, 4.7 eq) were employed. NMR yield: 65% (**8b-OMe**), 16% (**9b**) and 16% (**1b**). Product **8b-OMe** was isolated by chromatographic column on Al<sub>2</sub>O<sub>3</sub> using CH<sub>2</sub>Cl<sub>2</sub>:MeOH (95:5). Suitable crystals for X-ray diffraction analysis were obtained by slow diffusion of diethyl ether into a concentrated solution of **8b-OMe** in dichloromethane. Characterization data of compound **8b-OMe**: <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 8.77 (d, *J* = 5.0 Hz, 2H, CH<sub>pym</sub>), 7.71 (t, *J* = 7.8 Hz, 1H, CH<sub>Ar</sub>), 7.65 (t, *J* = 7.9 Hz, 1H, CH<sub>Ar</sub>), 7.57 (t, *J* = 5.0 Hz, 1H, CH<sub>pym</sub>), 7.43 (d, *J* = 7.9 Hz, 2H, CH<sub>Ar</sub>), 7.37 (d, *J* = 7.9 Hz, 2H, CH<sub>Ar</sub>), 7.19 – 7.15 (m, 2H, CH<sub>Ar</sub>), 6.90 – 6.86 (m, 2H, CH<sub>Ar</sub>), 3.80 (s, 3H, OCH<sub>3</sub>), 2.46 – 2.31 (m, 4H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.21 (dd, *J* = 6.8, 1.3 Hz, 12H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.10 (dd, *J* = 6.7, 1.4 Hz, 12H, CH(CH<sub>3</sub>)<sub>2</sub>). **HRMS (ESI+)**: calcd for C<sub>37</sub>H<sub>44</sub>ClN<sub>5</sub>O [M-Cl]<sup>+</sup>: *m/z* 574.3540; found: *m/z* 574.3547.



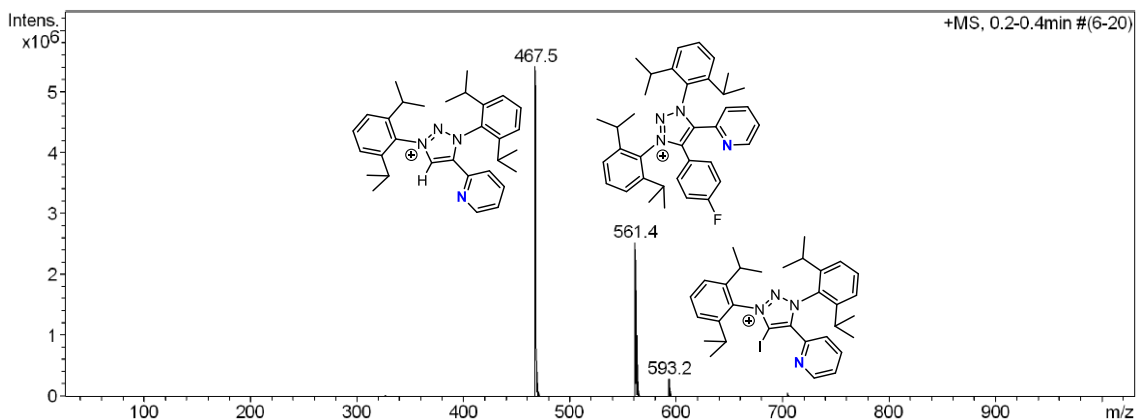
**Figure S2.** MS-ESI(+) of the reaction crude showing the peaks of **1b**, **8b-OMe** and **9b**.

**Reactivity of 2a with 4-iodotoluene.** Complex **2a** (10.4 mg, 0.015 mmol, 1 eq), [AgSbF<sub>6</sub>] (7.2 mg, 0.021 mmol, 1.4 eq) and 4-iodotoluene (17.0 mg, 0.078 mmol, 5.2 eq) were employed. NMR yield: 34% (**8a-Me**), 3% (**9a**), 31% (**1a**). Product **8a-Me** was isolated by chromatographic column on Al<sub>2</sub>O<sub>3</sub> using CH<sub>2</sub>Cl<sub>2</sub>:MeOH (95:5). Characterization data of compound **8a-Me**: <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 8.52 (d, *J* = 5.0 Hz, 1H), 7.77 (td, *J* = 7.9, 1.7 Hz, 1H), 7.70 (t, *J* = 7.9 Hz, 1H), 7.64 (t, *J* = 7.8 Hz, 1H), 7.45 – 7.40 (m, 3H), 7.38 – 7.34 (m, 3H), 7.20 (d, *J* = 8.1 Hz, 2H), 7.06 (d, *J* = 8.2 Hz, 2H), 2.43 – 2.33 (m, 7H), 1.21 (d, *J* = 6.8 Hz, 12H), 1.08 (d, *J* = 6.8 Hz, 12H). **HRMS (ESI+)**: calcd for C<sub>38</sub>H<sub>45</sub>F<sub>6</sub>N<sub>4</sub>Sb [M-SbF<sub>6</sub>]<sup>+</sup>: *m/z* 557.3639; found: *m/z* 557.3638.



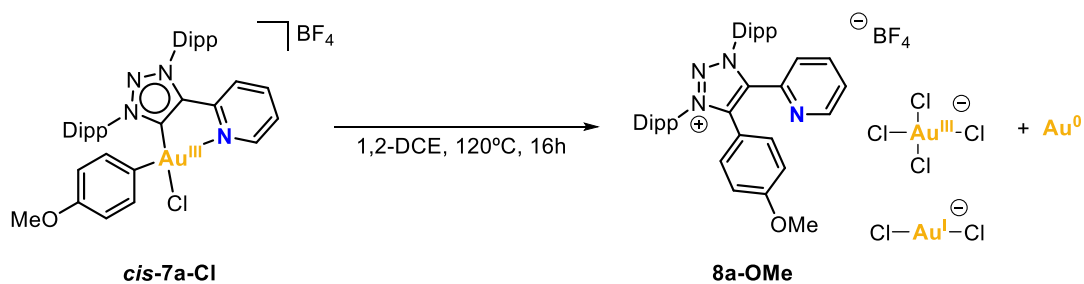
**Figure S3.** MS-ESI(+) of the reaction crude showing the peaks of **1a**, **8a-Me** and **9a**.

**Reactivity of 2a with 4-fluoriodobenzene.** Complex **2a** (9.9 mg, 0.014 mmol, 1 eq), [AgSbF<sub>6</sub>] (5.8 mg, 0.017 mmol, 1.2 eq) and 4-fluoriodobenzene (14.1 mg, 0.064 mmol, 4.5 eq) were employed. NMR yield: 12% (**8a-F**), traces (**9a**), 66% (**1a**).



**Figure S4.** MS-ESI(+) of the reaction crude showing the peaks of **1a**, **8a-F** and **9a**.

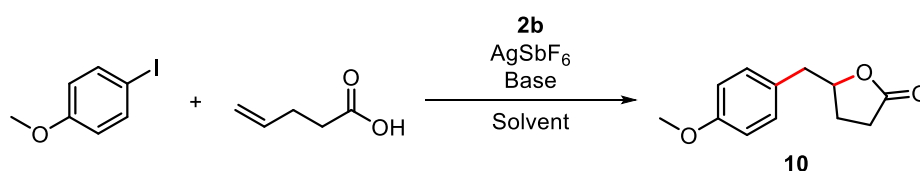
### 3.7 Reductive elimination from *cis*-**7a-Cl** to **8a-OMe**



**Scheme S8.** Reductive elimination from *cis*-**7a-Cl** to **8a-OMe**.

A vial was charged with *cis*-**7a-Cl** (11.7 mg, 0.013 mmol), 1,2-dichloroethane (0.5 mL) and a magnetic stirring bar, then was sealed under nitrogen atmosphere. The solution was heated at 120°C and stirred for 16h. After this time, a clear yellow solution with Au(0) precipitate was obtained. The volatiles were removed under vacuum, and the solid residue was analyzed by <sup>1</sup>H NMR. Product **8a-OMe** was obtained in 96% yield. <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 8.51 (ddd, *J* = 4.8, 1.8, 1.0 Hz, 1H, CH<sub>py</sub>), 7.78 (td, *J* = 7.8, 1.7 Hz, 1H, CH<sub>py</sub>), 7.70 (t, *J* = 7.9 Hz, 1H, CH<sub>Ar</sub>), 7.63 (t, *J* = 7.9 Hz, 1H, CH<sub>Ar</sub>), 7.44-7.39 (m, 4H: 2CH<sub>Ar</sub> and 2CH<sub>py</sub>), 7.36 (d, *J* = 7.9 Hz, 2H, CH<sub>Ar</sub>), 7.13-7.07 (m, 2H, CH<sub>Ar</sub>), 6.91-6.85 (m, 2H, CH<sub>Ar</sub>), 3.79 (s, 3H, OCH<sub>3</sub>), 2.40 (m, 4H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.21 (d, *J* = 6.9 Hz, 12H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.09 (dd, *J* = 6.7, 5.9 Hz, 12H, CH(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C NMR (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 163.3 (COCH<sub>3</sub>), 151.4 (CH<sub>py</sub>), 145.9 (C<sub>Ar</sub>, 4C), 143.4 (C<sub>trz</sub>), 142.4 (C<sub>py</sub>), 140.5 (C<sub>trz</sub>), 138.3 (CH<sub>py</sub>), 134.1 (CH<sub>Ar</sub>), 133.5 (CH<sub>Ar</sub>), 131.9 (CH<sub>Ar</sub>, 2C), 130.3 (C<sub>Ar</sub>), 129.5 (C<sub>Ar</sub>), 126.8 (CH<sub>py</sub>), 126.6 (CH<sub>py</sub>), 125.9 (CH<sub>Ar</sub>, 2C), 125.3 (CH<sub>Ar</sub>, 2C), 115.8 (CH<sub>Ar</sub>, 2C), 113.0 (C<sub>Ar</sub>), 56.2 (OCH<sub>3</sub>), 30.4 (CH(CH<sub>3</sub>)<sub>2</sub>, 2C), 30.3 (CH(CH<sub>3</sub>)<sub>2</sub>, 2C), 25.9 (CH(CH<sub>3</sub>)<sub>2</sub>, 2C), 25.5 (CH(CH<sub>3</sub>)<sub>2</sub>, 2C), 23.1 (CH(CH<sub>3</sub>)<sub>2</sub>, 2C), 22.9 (CH(CH<sub>3</sub>)<sub>2</sub>, 2C). **HRMS (ESI+)**: calcd for C<sub>38</sub>H<sub>45</sub>N<sub>4</sub>O<sup>+</sup> [M]<sup>+</sup>: *m/z* 573.3588; found: *m/z* 573.3586. **HRMS (ESI-)**: calcd for AuCl<sub>4</sub><sup>-</sup> [M]<sup>-</sup>: *m/z* 338.8390; found: *m/z* 338.8425; calcd for AuCl<sub>2</sub><sup>-</sup> [M]<sup>-</sup>: *m/z* 266.9043; found: *m/z* 266.9040.

#### 4. Optimization of the arylation-lactonization reaction of $\gamma$ -alkenoic acids



**Scheme S9.** Selected reaction to optimize the conditions for the arylation-lactonization of  $\gamma$ -alkenoic acids.

The reaction was carried under nitrogen atmosphere. A vial was charged with gold(I) complex **2b**, 4-iodoanisole, 4-pentenoic acid, a magnetic stirring bar, and the solvent of choice (0.4 mL), followed by the addition of a suspension of base and [AgSbF<sub>6</sub>] in the solvent of choice. The vial was sealed and heated at the desired temperature overnight. The yields were calculated by <sup>1</sup>H NMR using 1,3,5-trimethoxybenzene as internal standard.

**Table S1.** Optimization of the temperature

Entry	<b>2b</b> (mol%)	Temperature	P/(P+SM) (%) <sup>*</sup>
1	10	rt.	0
2	10	50	0
3 <sup>a</sup>	20	80	15

**Reaction conditions:** 4-iodoanisole (1 eq), 4-pentenoic acid (1 eq), K<sub>3</sub>PO<sub>4</sub> (1 eq), AgSbF<sub>6</sub> (1.5 eq), 1,2-dichloroethane, overnight. [4-iodoanisole] = 0.07M, V = 2 mL. <sup>a</sup>1.4 mL. \*P stands for the integral of one proton of the expected product **10** and SM stands for the integral of one proton of the remaining starting material (4-iodoanisole).

**Table S2.** Optimization of the base

Entry	AgSbF <sub>6</sub> (eq)	Base (eq.)	P/(P+SM) (%)
1	1.7	Li <sub>2</sub> CO <sub>3</sub> (1.2)	0
2	1.7	Na <sub>2</sub> CO <sub>3</sub> (1.2)	0
3	1.5	K <sub>2</sub> CO <sub>3</sub> (1.0)	0
4	1.6	Cs <sub>2</sub> CO <sub>3</sub> (1.2)	2
5	1.6	2,6-DTBP (1.0)	2
6	1.6	-	0

**Reaction conditions:** 4-iodoanisole (1 eq), 4-pentenoic acid (1 eq), **2b** (10 mol%), 1,2-dichloroethane, 80 °C, overnight. [4-iodoanisole] = 0.07M, V = 1.7 mL.

**Table S3.** Screening of conditions using stoichiometric amounts of gold complex **2b**

Entry	Iodoaryl (eq)	Acid (eq)	AgSbF <sub>6</sub> (eq)	K <sub>3</sub> PO <sub>4</sub> (eq)	Solvent	P/(P+SM) (%)	Conv. (%)	Yield (%)
1 <sup>a*</sup>	1	1	1	1	1,2-DCE	0	nc	0
2 <sup>a</sup>	1	1	1	1.1	1,2-DCE	15	nc	nc
3 <sup>b</sup>	1	1	2.3	1.6	1,2-DCE	25	nc	nc
4	1	1	3.6	1	1,2-DCE	15	nc	nc
5	1	1	2.4	1.5	DCM	29	nc	nc
6	1	1	4.4	1.4	DCM	0	nc	0
7	5	1	6.6	1.4	1,2-DCE	0	nc	0
8	1	5	2.7	1.2	1,2-DCE	49	nc	nc
9 <sup>**</sup>	1	5	2.8	1.8	1,2-DCE	17	nc	nc
10 <sup>c</sup>	1	5	2.5	7.2	1,2-DCE	0	nc	0
11 <sup>d</sup>	1	10	2.7	1.2	1,2-DCE	38	nc	nc
12	1	5	2.8	1	TFE	88	92	63
13 <sup>***</sup>	1	5	2.6	1.2	TFE	>99	>99	67

**Reaction conditions:** Complex **2b** (1 eq), 80 °C, overnight. [4-iodoanisole] = 0.02M, V = 1 mL. <sup>a</sup>1.4 mL, <sup>b</sup>2 mL, <sup>c</sup>0.85 mL, <sup>d</sup>0.6 mL. \*Blank experiment without **2b**, \*\*70 °C, \*\*\*100 °C. The notation “nc” stands for “not calculated”.

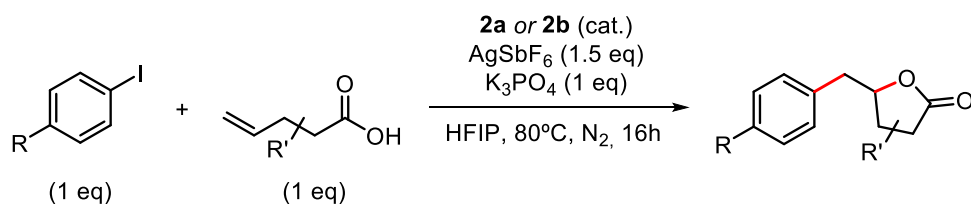


**Table S4.** Optimization of the solvent using substoichiometric amounts of complex **2b**

Entry	<b>2b</b> (mol%)	AgSbF <sub>6</sub> (eq)	K <sub>3</sub> PO <sub>4</sub> (eq)	Solvent	P/(P+SM) (%)	Conv. (%)	Yield (%)
1	10	1.5	1.0	DMF	0	nc	0
2	10	1.5	1.2	toluene	0	nc	0
3	10	1.6	1.2	THF	0	nc	0
4	10	1.6	1.2	DCM	9	nc	nc
5	10	1.5	1.0	DMSO	0	nc	0
6	10	1.6	1.1	MeCN	0	nc	0
7	10	1.5	1.0	TFE	18	nc	nc
8	10	1.5	0.5	TFE	32	51	24
9*	10	1.5	1.0	TFE	37	51	28
10**	10	1.5	1.1	TFE	25	54	15
11 <sup>a**</sup>	40	2.0	1.1	TFE	80	79	44
12 <sup>b**</sup>	70	2.2	1.2	TFE	87	81	65
13 <sup>a**</sup>	1	1.1	0.5	TFE	2	38	1.6
14 <sup>c</sup>	10	1.5	1.0	HFIP	40	56	29

**Reaction conditions:** 4-iodoanisole (1 eq), 4-pentenoic acid (1 eq), 80 °C, overnight, solvent ([4-iodoanisole] = 0.08M), V = 1.4 mL. <sup>a</sup>0.65 mL, <sup>b</sup>0.55 mL, <sup>c</sup>1 mL. \*100 °C. \*\*24 h. The notation “nc” stands for “not calculated”.

## 5. Scope of the arylation-lactonization reaction of $\gamma$ -alkenoic acids



**Scheme S10.** Selected reaction conditions for the gold-catalyzed arylation-lactonization of  $\gamma$ -alkenoic acids.

**Table S5.** Scope of the gold-catalyzed arylation-lactonization of  $\gamma$ -alkenoic acids towards the formation of products **10** – **16**.

Entry	R	Acid	Catalyst (mol%)	Product	Conv. (%)	Yield (%)
1	OMe		<b>2a</b> (10)	<b>10</b>	78	35
2	OMe		<b>2b</b> (10)	<b>10</b>	56	29
3	OMe		<b>2a</b> (20)	<b>10</b>	-	33*
4	H		<b>2a</b> (10)	<b>11</b>	nc	31
5	H		<b>2b</b> (10)	<b>11</b>	nc	50
6	H		<b>2b</b> (20)	<b>11</b>	nc	87
7	H		-	<b>11</b>	nc	0
8	Me		<b>2a</b> (10)	<b>12</b>	95	60
9	Me		<b>2b</b> (10)	<b>12</b>	98	81
10	CF <sub>3</sub>		<b>2a</b> (10)	<b>13</b>	nc	13
11	CF <sub>3</sub>		<b>2b</b> (10)	<b>13</b>	nc	11
12	NO <sub>2</sub>		<b>2a</b> (10)	<b>14</b>	12	1
13	NO <sub>2</sub>		<b>2b</b> (10)	<b>14</b>	5	1
14	OMe		<b>2a</b> (10)	<b>15</b>	49	37
15	OMe		<b>2b</b> (10)	<b>15</b>	67	41
16	OMe		<b>2a</b> (20)	<b>15</b>	-	25*
17	OMe		<b>2a</b> (10)	<b>16</b>	60	32
18	OMe		<b>2b</b> (10)	<b>16</b>	45	18
19	OMe		<b>2a</b> (20)	<b>16</b>	-	29*

Conversions and yields were calculated by <sup>1</sup>H NMR using 1,3,5-trimethoxybenzene as internal standard. \*Isolated yield. Conversions are labeled as “nc” (not calculated) in those cases where volatile iodoaryl substrates were employed.

**Synthesis of 10.** For the synthesis of **10** was employed 4-iodoanisole (99.7 mg, 0.43 mmol, 1.0 eq), 4-pentenoic acid (45  $\mu$ L, 0.44 mmol, 1.0 eq), **2a** (60.0 mg, 0.09 mmol, 0.2 eq), [AgSbF<sub>6</sub>] (226.6 mg, 0.66 mmol, 1.5 eq), K<sub>3</sub>PO<sub>4</sub> (57.2 mg, 0.42 mmol, 1.0 eq), and HFIP (5 mL). The reaction mixture was heated in a sealed vial at 80°C for 16h. The reaction crude was filtered, and all volatiles were removed under high vacuum. The residue was purified by column chromatography using hexane:EtOAc (9:1). Compound **10** was obtained as a yellow oil. Yield: 28.6 mg (33%). The <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra matched with those reported in the literature.<sup>7</sup>

**Synthesis of 11.** For the synthesis of **11** was employed iodobenzene (9.3  $\mu$ L, 0.08 mmol, 1.0 eq), 4-pentenoic acid (8.5  $\mu$ L, 0.08 mmol, 1.0 eq), catalyst **2a** or **2b** (10 mol% or 20 mol%), [AgSbF<sub>6</sub>] (0.13 mmol, 1.5 eq), K<sub>3</sub>PO<sub>4</sub> (0.08 mmol, 1.0 eq), and HFIP (1 mL). The reaction mixture was heated in a sealed vial at 80°C for 16h. The reaction crude was filtered, and all volatiles were removed under high vacuum. The yield of product **11** was determined by <sup>1</sup>H NMR using 1,3,5-trimethoxybenzene as internal standard. Yield: 31% (employing **2a** 10 mol%), 50% (employing **2b** 10 mol%), 87% (employing **2b** 20 mol%). Out of the <sup>1</sup>H NMR of the crude, the signals of product **11** could be identified as they matched with the characterization reported in the literature.<sup>8</sup>

**Synthesis of 12.** For the synthesis of **12** was employed 4-iodotoluene (18.8 mg, 0.09 mmol, 1.0 eq), 4-pentenoic acid (9.0  $\mu$ L, 0.09 mmol, 1.0 eq), catalyst **2a** or **2b** (10 mol%), [AgSbF<sub>6</sub>] (0.13 mmol, 1.5 eq), K<sub>3</sub>PO<sub>4</sub> (0.08 mmol, 1.0 eq), and HFIP (1 mL). The reaction mixture was heated in a sealed vial at 80°C for 16h. The reaction crude was filtered, and all volatiles were removed under high vacuum. The yield of product **12** was determined by <sup>1</sup>H NMR using 1,3,5-trimethoxybenzene as internal standard. Yield: 60% (employing **2a**), 81% (employing **2b**). Out of the <sup>1</sup>H NMR of the crude, the signals of product **12** could be identified as they matched with the characterization reported in the literature.<sup>9</sup>

**Synthesis of 13.** For the synthesis of **13** was employed 4-iodobenzotrifluoride (12.3  $\mu$ L, 0.08 mmol, 1.0 eq), 4-pentenoic acid (8.5  $\mu$ L, 0.08 mmol, 1.0 eq), catalyst **2a** or **2b** (10 mol%), [AgSbF<sub>6</sub>] (0.13 mmol, 1.5 eq), K<sub>3</sub>PO<sub>4</sub> (0.08 mmol, 1.0 eq), and HFIP (1 mL). The reaction mixture was heated in a sealed vial at 80°C for 16h. The reaction crude was filtered, and all volatiles were removed under high vacuum. The yield of product **13** was determined by <sup>1</sup>H NMR using 1,3,5-trimethoxybenzene as internal standard. Yield: 13% (employing **2a**), 11% (employing **2b**). Out of the <sup>1</sup>H NMR of the crude, the signals of product **13** could be identified as they matched with the characterization reported in the literature.<sup>9</sup>

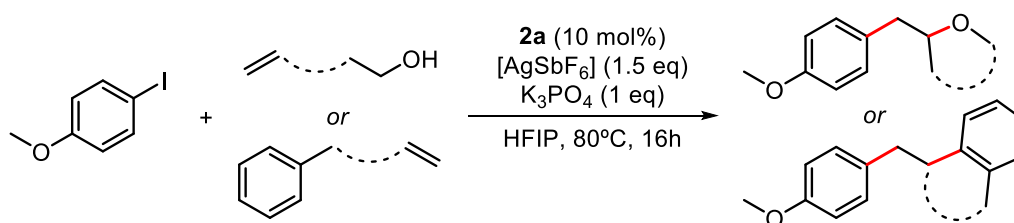
**Synthesis of 14.** For the synthesis of **14** was employed 1-iodo-4-nitrobenzene (21.7 mg, 0.09 mmol, 1.0 eq), 4-pentenoic acid (8.9  $\mu$ L, 0.09 mmol, 1.0 eq), catalyst **2a** or **2b** (10 mol%), [AgSbF<sub>6</sub>] (0.13 mmol, 1.5 eq), K<sub>3</sub>PO<sub>4</sub> (0.09 mmol, 1.0 eq), and HFIP (1 mL). The reaction mixture was heated in a sealed vial at 80°C for 16h. The reaction crude was filtered, and all volatiles were removed under high vacuum. The yield of product **14** was determined by <sup>1</sup>H NMR using 1,3,5-trimethoxybenzene as internal standard. Yield: 1% (employing **2a**), 1% (employing **2b**).

**Synthesis of 15.** For the synthesis of **15** was employed 4-iodoanisole (56.5 mg, 0.24 mmol, 1.0 eq), 2,2-dimethylpent-4-enoic acid (33  $\mu$ L, 0.24 mmol, 1.0 eq), **2a** (34.2 mg,

0.05 mmol, 0.2 eq), [AgSbF<sub>6</sub>] (124.0 mg, 0.36 mmol, 1.5 eq), K<sub>3</sub>PO<sub>4</sub> (32.5 mg, 0.24 mmol, 1.0 eq), and HFIP (2.6 mL). The reaction mixture was heated in a sealed vial at 80°C for 16h. The reaction crude was filtered, and all volatiles were removed under high vacuum. Then, ethyl acetate was added to the oily residue and the solution was filtered through a basic alumina plug. The product was isolated from preparative TLC using pentane:EtOAc (8:2). Compound **15** was obtained as a pale yellow oil. Yield: 14.4 mg (25%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.16 – 7.13 (m, 2H, CH<sub>Ar</sub>), 6.87 – 6.83 (m, 2H, CH<sub>Ar</sub>), 4.59 (dq, *J* = 9.9, 6.2 Hz, 1H, CH<sub>Alk</sub>), 3.79 (s, 3H, OCH<sub>3</sub>), 3.04 (dd, *J* = 14.0, 6.4 Hz, 1H, CH<sub>2</sub>), 2.82 (dd, *J* = 14.0, 6.3 Hz, 1H, CH<sub>2</sub>), 2.06 (dd, *J* = 12.7, 5.9 Hz, 1H, CH<sub>2</sub>), 1.80 (dd, *J* = 12.8, 9.9 Hz, 1H, CH<sub>2</sub>), 1.23 (s, 3H, CH<sub>3</sub>), 1.22 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 181.9 (C=O), 158.7 (C<sub>Ar</sub>), 130.5 (CH<sub>Ar</sub>, 2C), 128.3 (C<sub>Ar</sub>), 114.1 (CH<sub>Ar</sub>, 2C), 77.6 (CH<sub>Alk</sub>), 55.4 (OCH<sub>3</sub>), 43.0 (CH<sub>2</sub>), 40.8 (C<sub>Alk</sub>), 40.6 (CH<sub>2</sub>), 25.1 (CH<sub>3</sub>), 24.6 (CH<sub>3</sub>). HRMS (ESI<sup>+</sup>): calcd for C<sub>14</sub>H<sub>18</sub>O<sub>3</sub> [M+Na]<sup>+</sup>: *m/z* 257.1148; found: *m/z* 257.1143.

**Synthesis of 16.** For the synthesis of **16** was employed 4-iodoanisole (99.6 mg, 0.43 mmol, 1.0 eq), freshly prepared 3,3-dimethylpent-4-enoic acid<sup>10</sup> (63 μL, 0.43 mmol, 1.0 eq), **2a** (60.8 mg, 0.09 mmol, 0.2 eq), [AgSbF<sub>6</sub>] (222.3 mg, 0.65 mmol, 1.5 eq), K<sub>3</sub>PO<sub>4</sub> (59.5 mg, 0.44 mmol, 1.0 eq), and HFIP (5 mL). The reaction mixture was heated in a sealed vial at 80°C for 16h. The reaction crude was filtered, and all volatiles were removed under high vacuum. Then, ethyl acetate was added to the oily residue and the solution was filtered through a basic alumina plug. The product was isolated from column chromatography using hexane:EtOAc (9:1). Compound **16** was obtained as a white solid. Colorless crystals suitable for X-ray diffraction were obtained by evaporation of a concentrated solution of **16** in methanol. Yield: 29.3 mg (29%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.20 – 7.16 (m, 2H, CH<sub>Ar</sub>), 6.86 – 6.83 (m, 2H, CH<sub>Ar</sub>), 4.25 (dd, *J* = 9.3, 3.7 Hz, 1H, CH<sub>Alk</sub>), 3.78 (s, 3H, OCH<sub>3</sub>), 2.84 (dd, *J* = 14.6, 9.3 Hz, 1H, CH<sub>2</sub>), 2.76 (dd, *J* = 14.6, 3.8 Hz, 1H, CH<sub>2</sub>), 2.41 (d, *J* = 16.9 Hz, 1H, CH<sub>2</sub>), 2.32 (d, *J* = 16.8 Hz, 1H, CH<sub>2</sub>), 1.13 (s, 3H, CH<sub>3</sub>), 1.12 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 176.0 (C=O), 158.5 (C<sub>Ar</sub>), 130.2 (CH<sub>Ar</sub>, 2C), 129.7 (C<sub>Ar</sub>), 114.1 (CH<sub>Ar</sub>, 2C), 89.7 (CH<sub>Alk</sub>), 55.4 (OCH<sub>3</sub>), 45.0 (CH<sub>2</sub>), 39.6 (C<sub>Alk</sub>), 34.7 (CH<sub>2</sub>), 25.2 (CH<sub>3</sub>), 21.5 (CH<sub>3</sub>). HRMS (ESI<sup>+</sup>): calcd for C<sub>14</sub>H<sub>18</sub>O<sub>3</sub> [M+Na]<sup>+</sup>: *m/z* 257.1148; found: *m/z* 257.1139. Calcd for C<sub>14</sub>H<sub>18</sub>O<sub>3</sub> [2M+Na]<sup>+</sup>: *m/z* 491.2404; found: *m/z* 491.2385.

## 6. Au(I)-catalyzed oxyarylation and 1,2-diarylation reactions of alkenes



**Scheme S11.** Oxyarylation and 1,2-diarylation reactions of alkenes catalyzed by complex **2a**.

The catalytic performance of Au(I) complex **2a** was tested in the oxyarylation and 1,2-diarylation reactions of olefins, under the previously optimized reaction conditions, using 4-iodoanisole as the aryl iodide counterpart (Scheme S11).

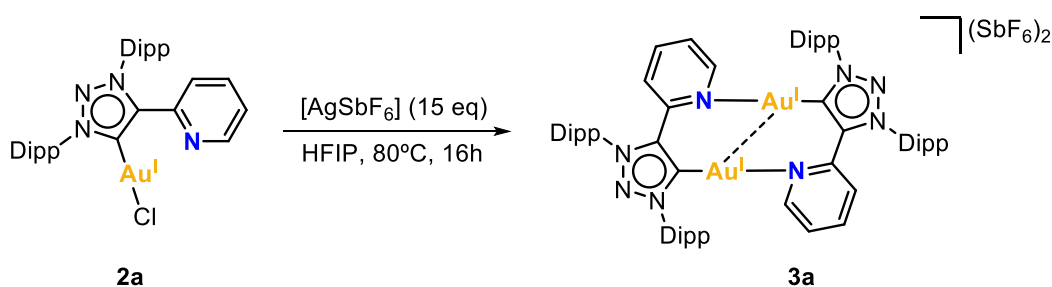
Under nitrogen atmosphere, a vial was charged with 4-iodoanisole (0.09 mmol, 1.0 eq), the alkene (0.09 mmol, 1.0 eq), catalyst **2a** (10 mol%), [AgSbF<sub>6</sub>] (0.13 mmol, 1.5 eq), K<sub>3</sub>PO<sub>4</sub> (0.09 mmol, 1.0 eq), and HFIP (1 mL). The vial was sealed and heated at 80°C for 16h. The reaction crude was filtered, and all volatiles were removed under high vacuum. The yield of the desired product was determined by <sup>1</sup>H NMR using 1,3,5-trimethoxybenzene as internal standard and according to the NMR characterization found in the literature.<sup>11</sup> The reactions tested are displayed in Table S6.

**Table S6.** Summary of the **2a**-catalyzed oxyarylation and 1,2-diarylation reactions of alkenes.

Entry	Alkene	Product	Yield (%)
1			18
2			25
3			5
4			0

## 7. Mechanistic studies

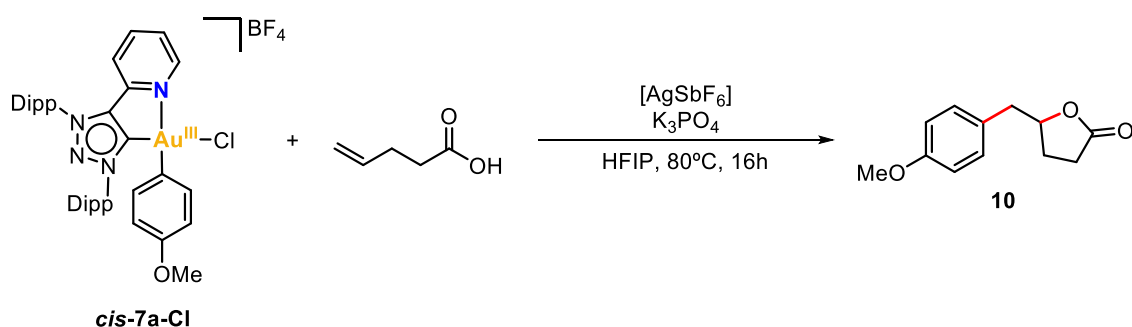
### 7.1 Role of the silver salt



**Scheme S12.** Reactivity of **2a** with AgSbF<sub>6</sub> under the reaction conditions optimized for the arylation-lactonization catalysis.

Under nitrogen, a vial was charged with **2a** (8.0 mg, 0.011 mmol, 1.0 eq), [AgSbF<sub>6</sub>] (60.5 mg, 0.176 mmol, 15.4 eq), and a stirring bar. Then, HFIP (1 mL) was added, and the vial was sealed. The mixture was stirred and heated at 80°C for 16h. The reaction conditions simulated the conditions used in the arylation-lactonization catalysis in terms of solvent, time, temperature, and ratio [Au]:Ag<sup>+</sup> (1:15). The reaction crude was filtered, and the volatiles were removed under vacuum. NMR analysis revealed that dimer **3a** was quantitatively formed. MS (ESI+) analysis showed a unique peak at *m/z* 704.3 corresponding to [(MIC<sup>N<sup>py</sup></sup>)Au<sup>I</sup> + MeCN]<sup>+</sup>.

## 7.2 Stoichiometric reaction from complex *cis-7a-Cl* to product **10**



**Scheme S13.** Stoichiometric reaction of *cis-7a-Cl* towards the formation of product **10**.

In a glovebox, a vial was charged with complex *cis-7a-Cl* (7.0 mg, 0.008 mmol, 1.0 eq), [AgSbF<sub>6</sub>] (3.2 mg, 0.009 mmol, 1.2 eq), K<sub>3</sub>PO<sub>4</sub> (1.1 mg, 0.008 mmol, 1.0 eq) and a stirring bar. Outside the glovebox and under nitrogen atmosphere, a freshly solution of 4-pentenoic acid (1.0 μL, 0.010 mmol, 1.3 eq) in HFIP (0.8 mL) was added to the reaction mixture. The vial was sealed, stirred, and heated at 80°C for 16h. After this time, the white suspension was filtered, and the volatiles were removed under vacuum. NMR analysis of the solid residue revealed the formation of product **10** in 73% yield (NMR yield using mesitylene as internal standard). MS (ESI+) analysis showed a peak at *m/z* 207.0 corresponding to the [M+H]<sup>+</sup> species of product **10**, and a peak at *m/z* 704.4 corresponding to [(MIC<sup>N<sup>py</sup></sup>)Au<sup>I</sup> + MeCN]<sup>+</sup>.

## 8. NMR and HRMS-ESI spectra

### 8.1 NMR and HRMS-ESI Spectra of triazolium salt 1a

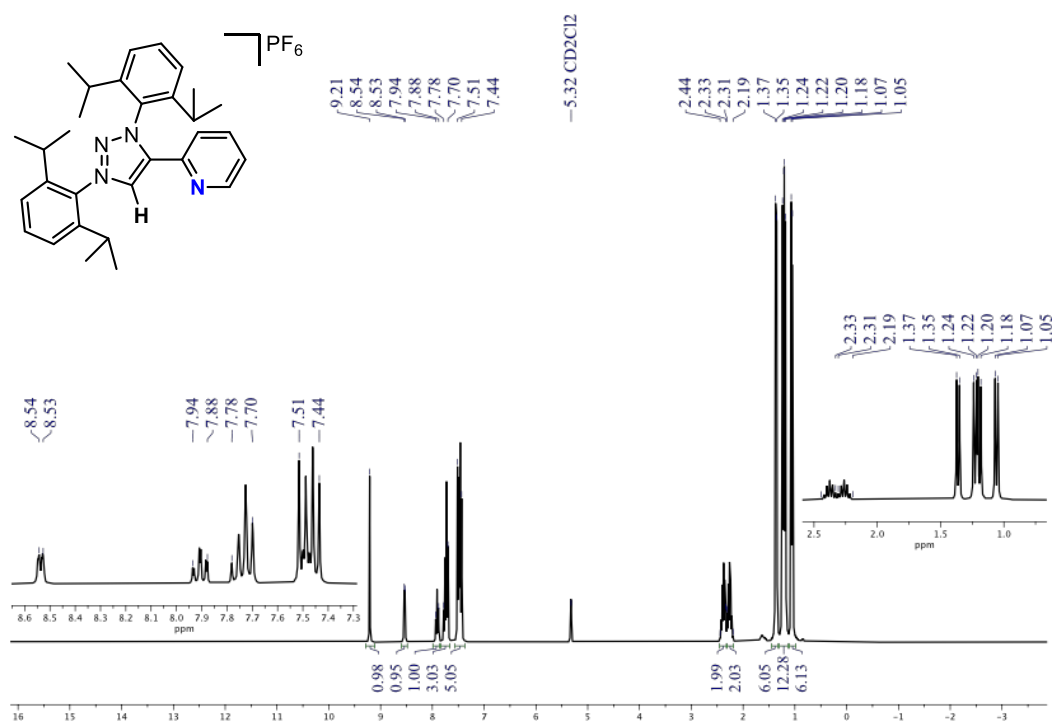


Figure S5.  $^1\text{H}$  NMR (400MHz, 298K) of 1a in  $\text{CD}_2\text{Cl}_2$ .

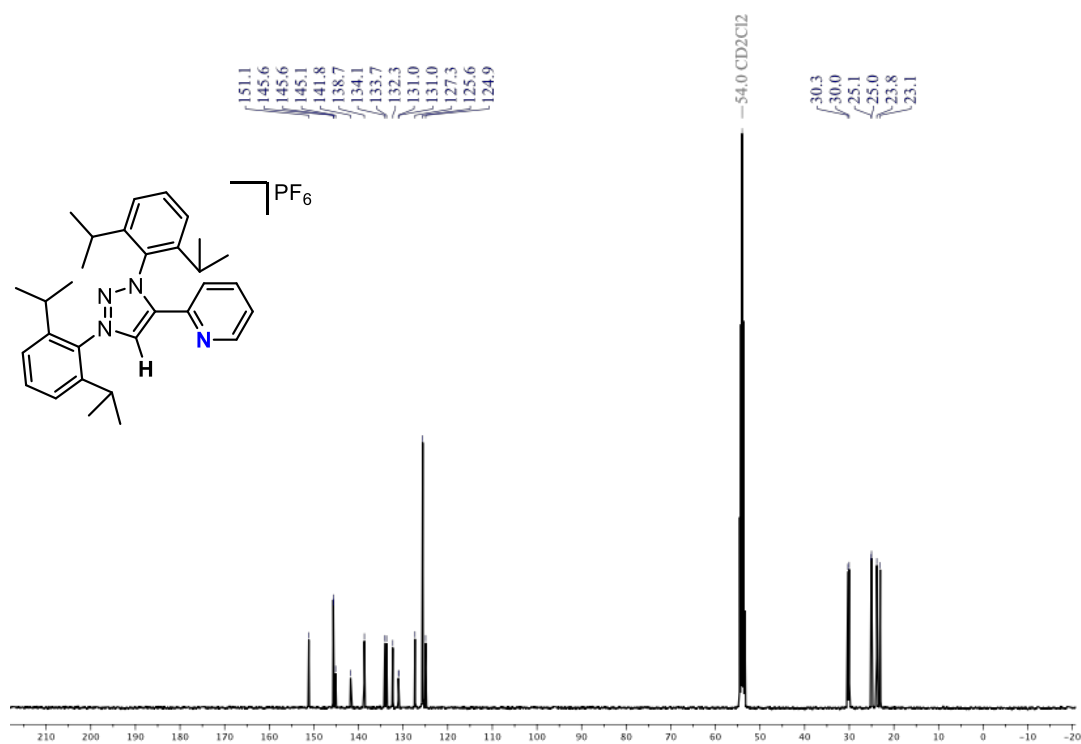


Figure S6.  $^{13}\text{C}$  NMR (100MHz, 298K) of 1a in  $\text{CD}_2\text{Cl}_2$ .

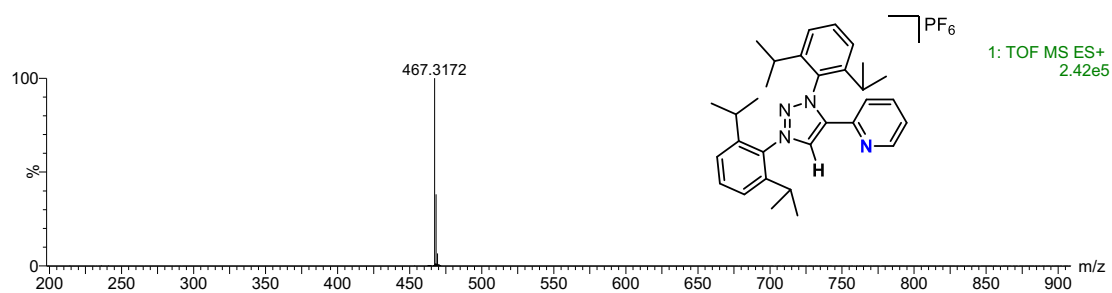


Figure S7. HRMS-ESI(+) of **1a**.

## 8.2 NMR and HRMS-ESI Spectra of triazolium salt **1b**

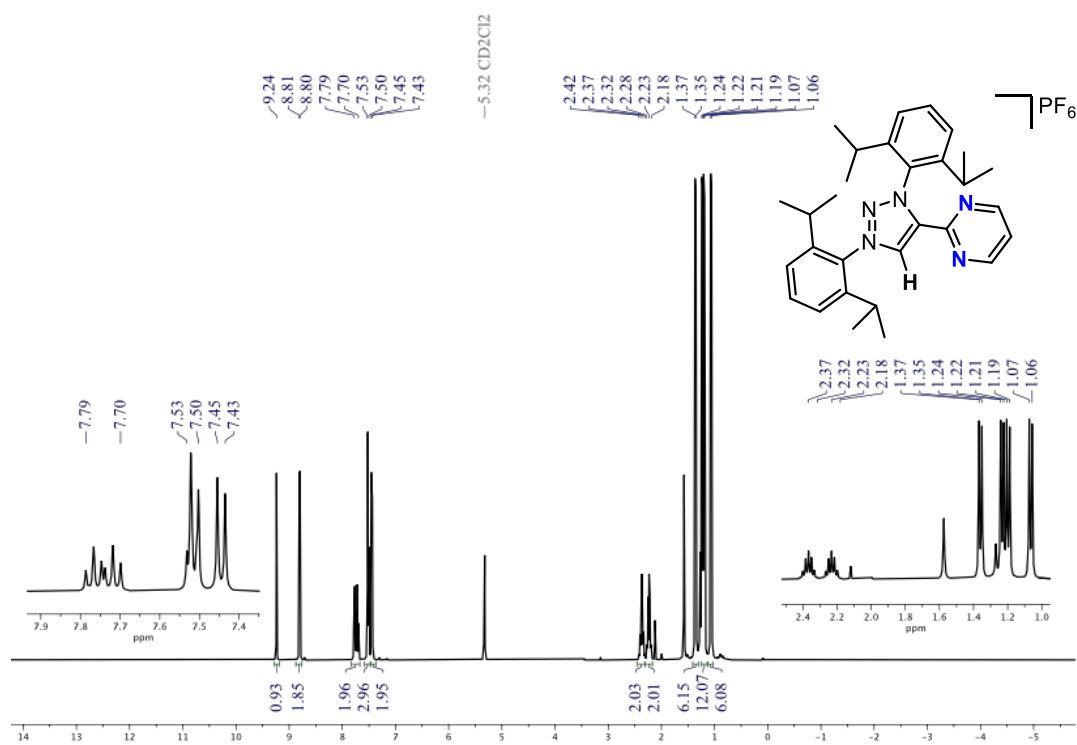
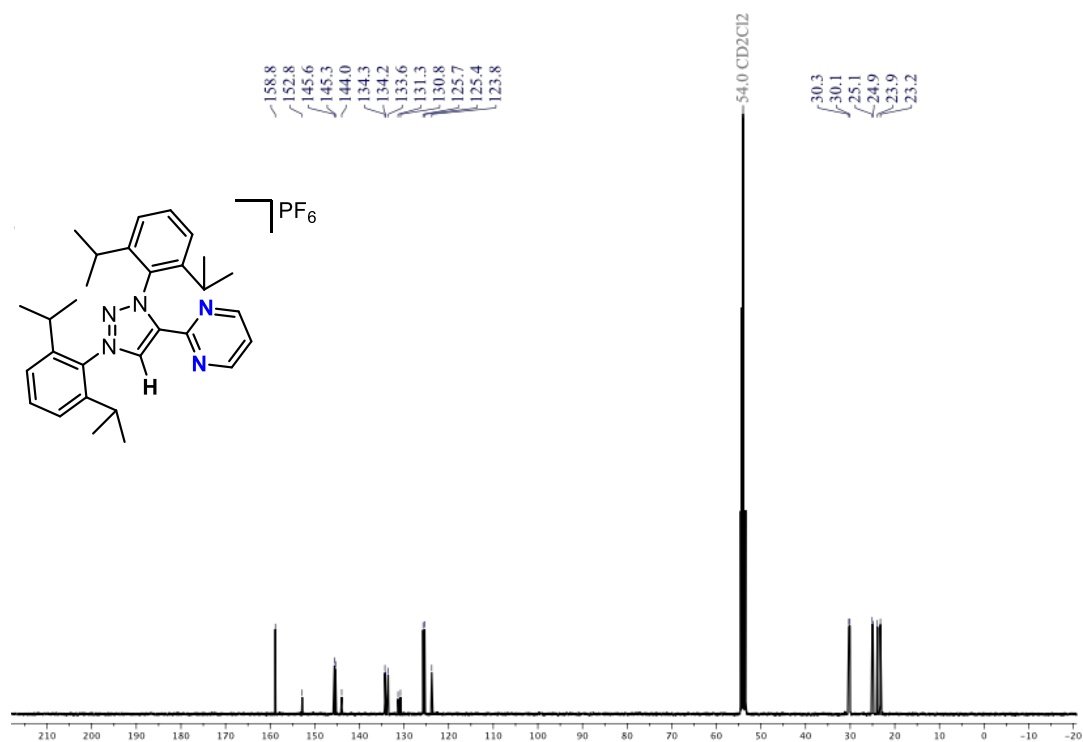
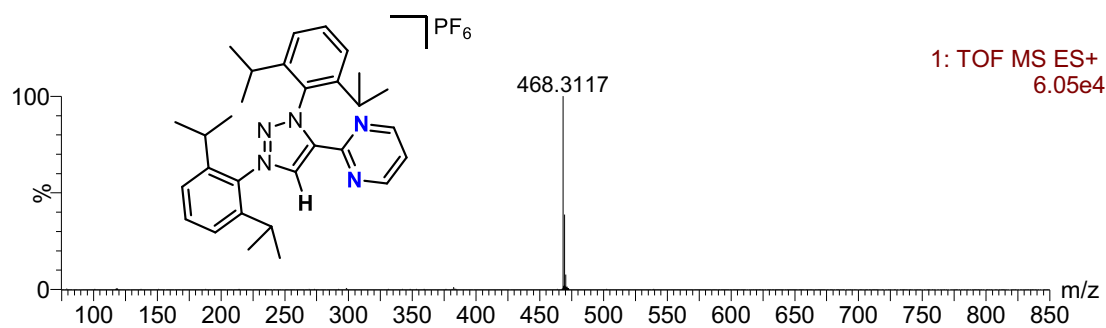


Figure S8.  $^1\text{H}$  NMR (400MHz, 298K) of **1b** in  $\text{CD}_2\text{Cl}_2$ .





**Figure S9.**  $^{13}\text{C}$  NMR (100MHz, 298K) of **1b** in  $\text{CD}_2\text{Cl}_2$ .



**Figure S10.** HRMS-ESI(+) of **1b**.

### 8.3 NMR Spectra of complex 2a

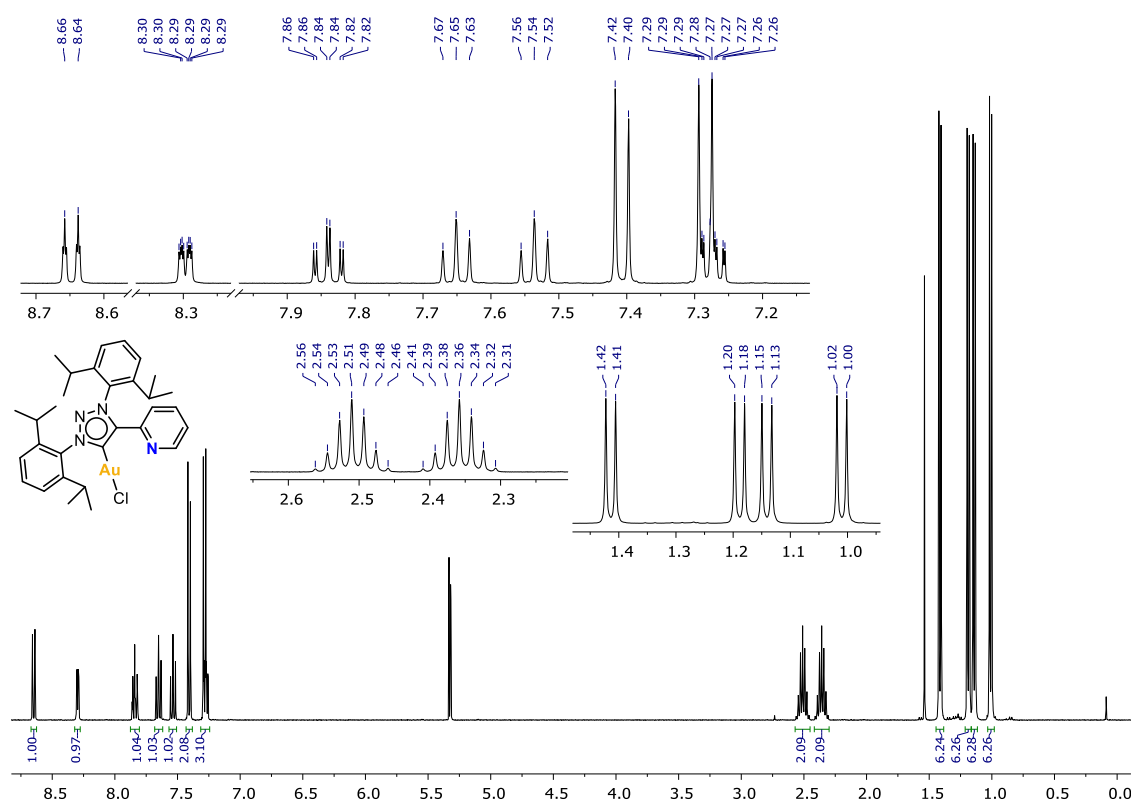


Figure S11. <sup>1</sup>H NMR (400MHz, 298K) of 2a in CD<sub>2</sub>Cl<sub>2</sub>.

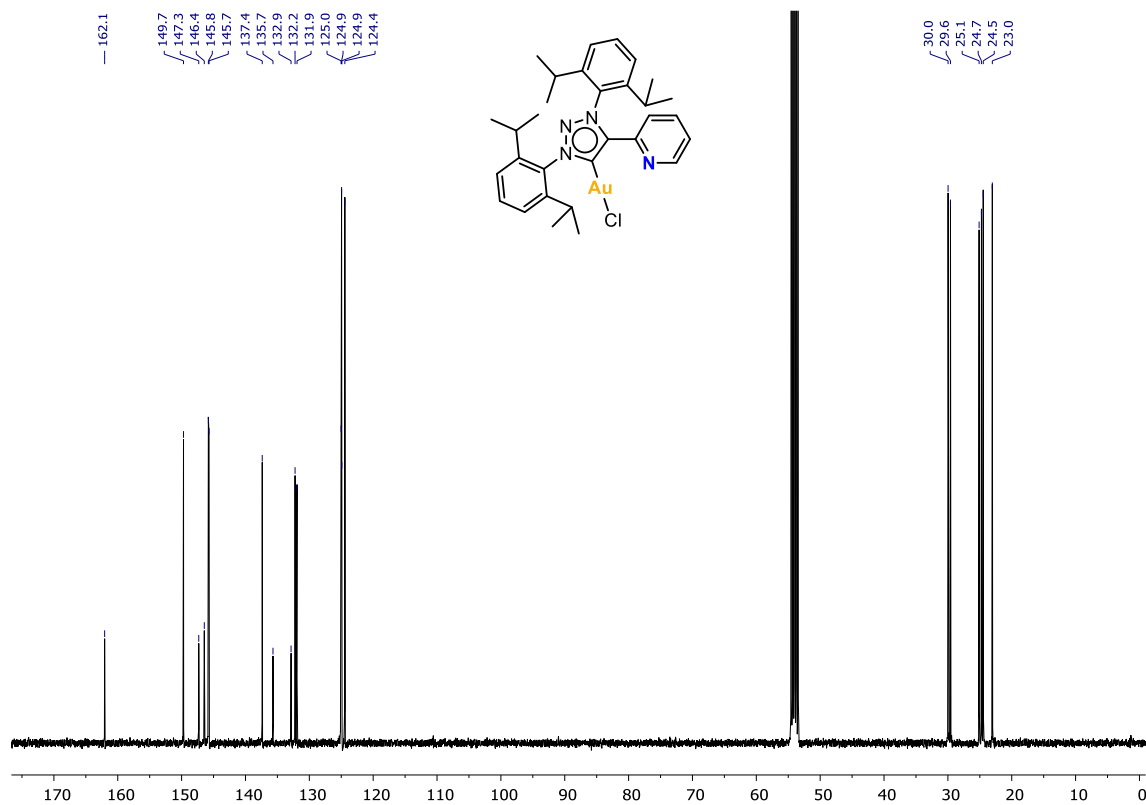
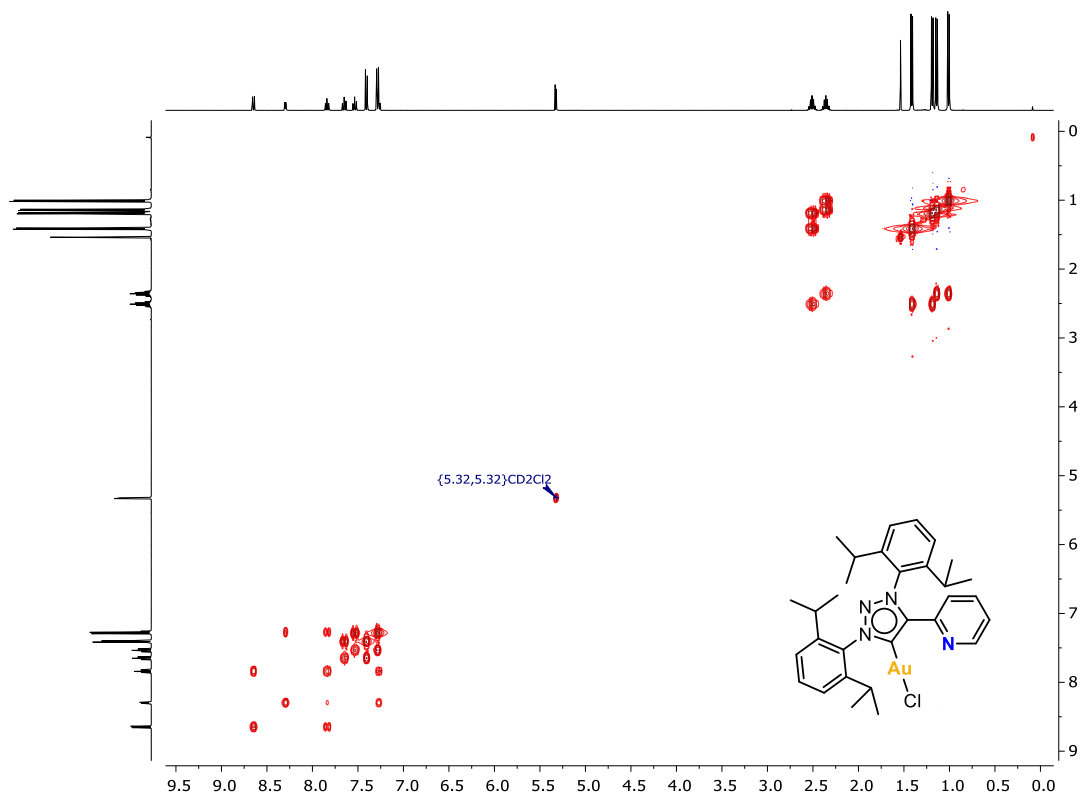
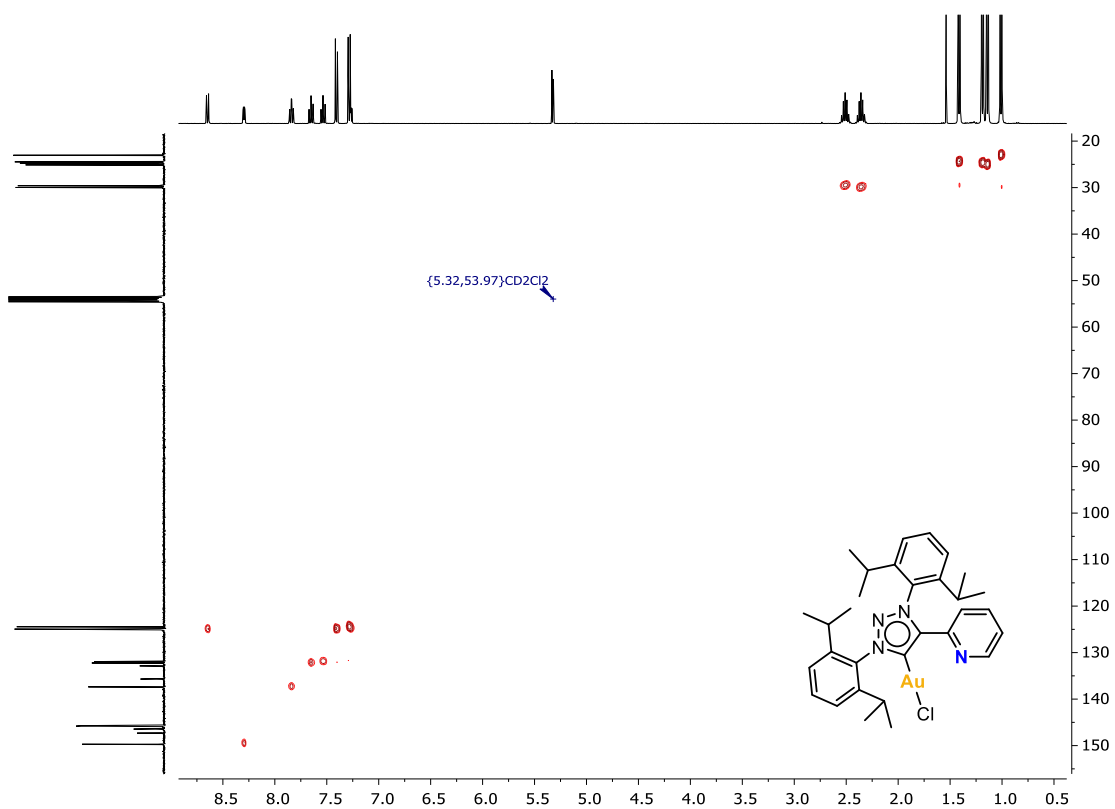


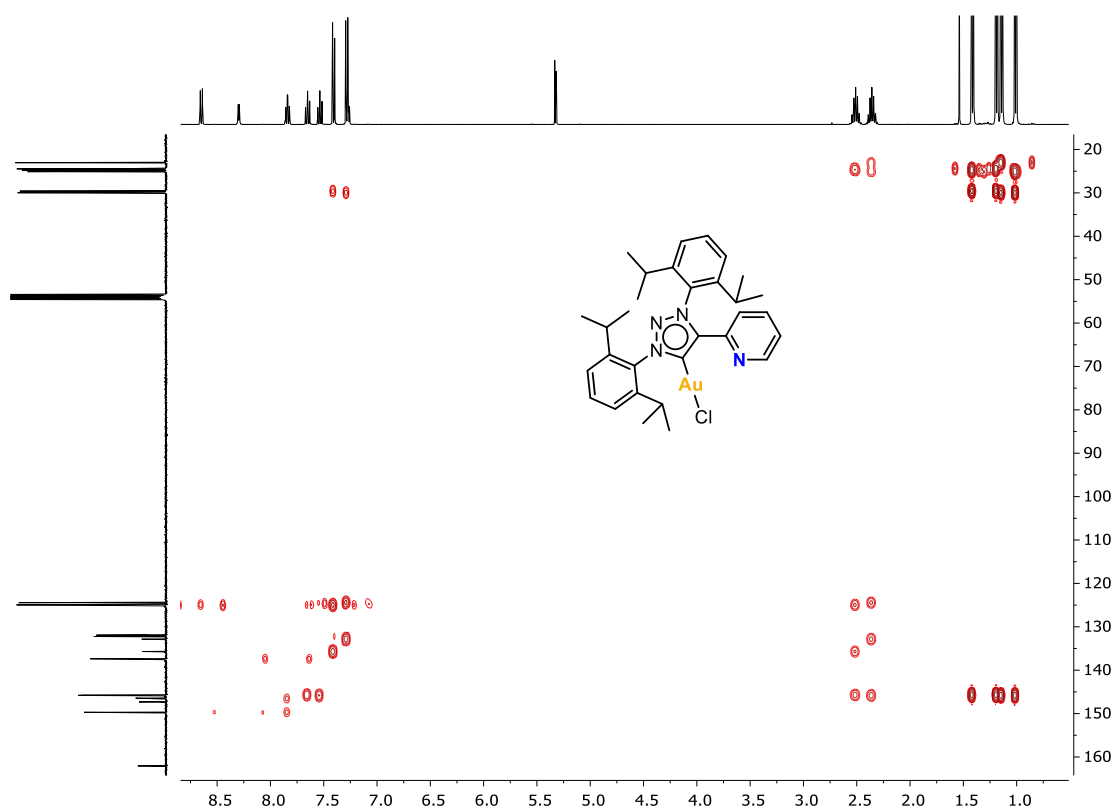
Figure S12. <sup>13</sup>C NMR (101MHz, 298K) of 2a in CD<sub>2</sub>Cl<sub>2</sub>.



**Figure S13.**  $^1\text{H}$ ,  $^1\text{H}$ -COSY NMR (400MHz, 298K) of **2a** in  $\text{CD}_2\text{Cl}_2$ .

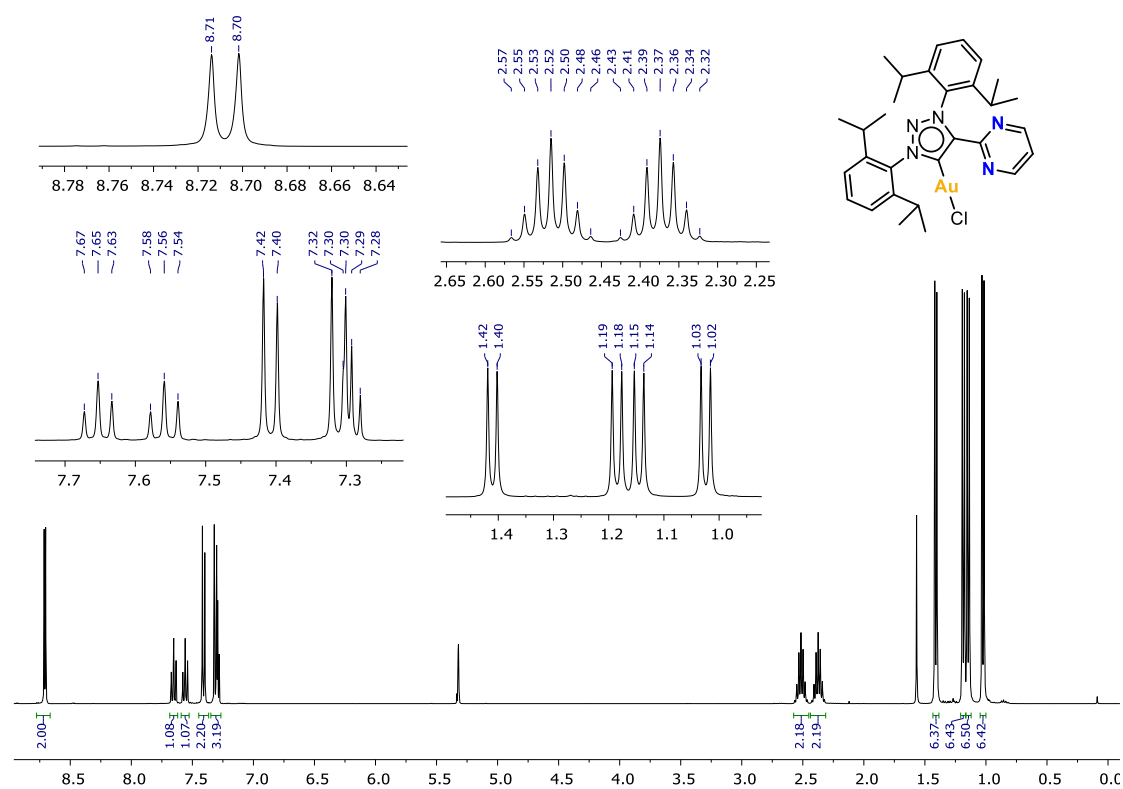


**Figure S14.**  $^1\text{H}$ ,  $^{13}\text{C}$ -HSQC NMR (400MHz, 298K) of **2a** in  $\text{CD}_2\text{Cl}_2$ .

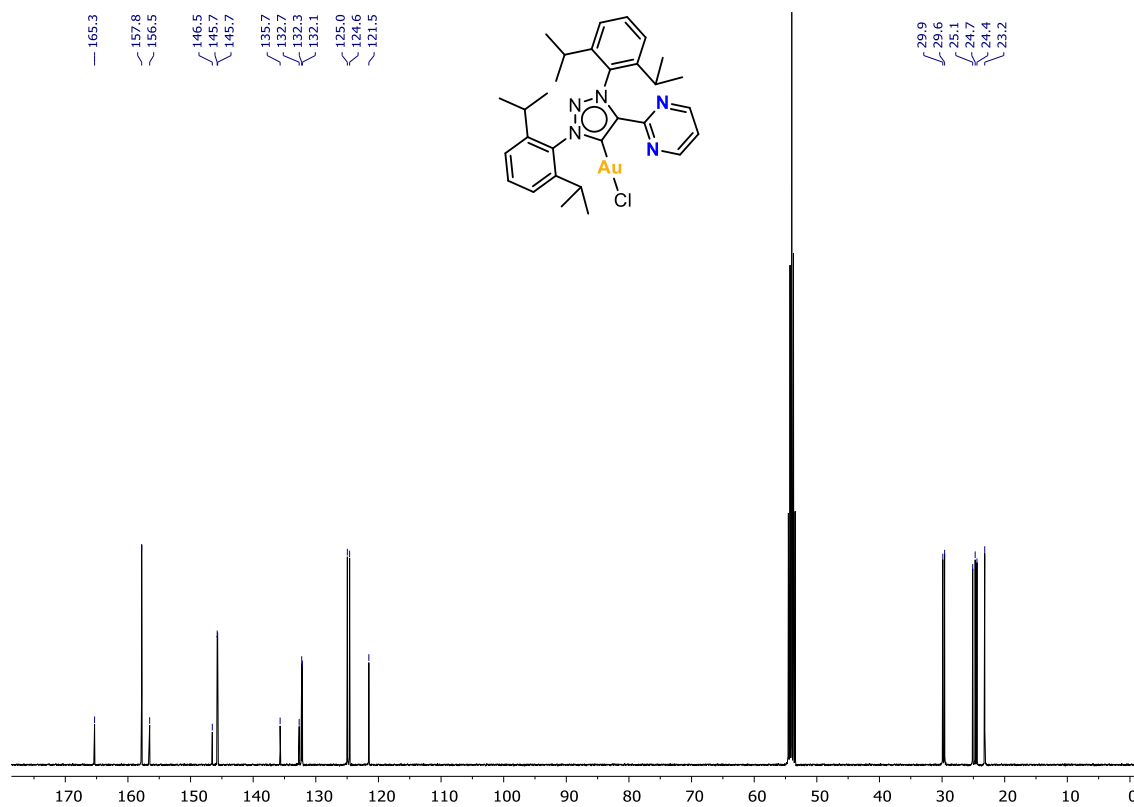


**Figure S15.**  $^1\text{H}$ ,  $^{13}\text{C}$ -HMBC NMR (400MHz, 298K) of **2a** in  $\text{CD}_2\text{Cl}_2$ .

## 8.4 NMR Spectra of complex **2b**



**Figure S16.** <sup>1</sup>H NMR (400MHz, 298K) of **2b** in CD<sub>2</sub>Cl<sub>2</sub>.



**Figure S17.** <sup>13</sup>C NMR (101MHz, 298K) of **2b** in CD<sub>2</sub>Cl<sub>2</sub>.

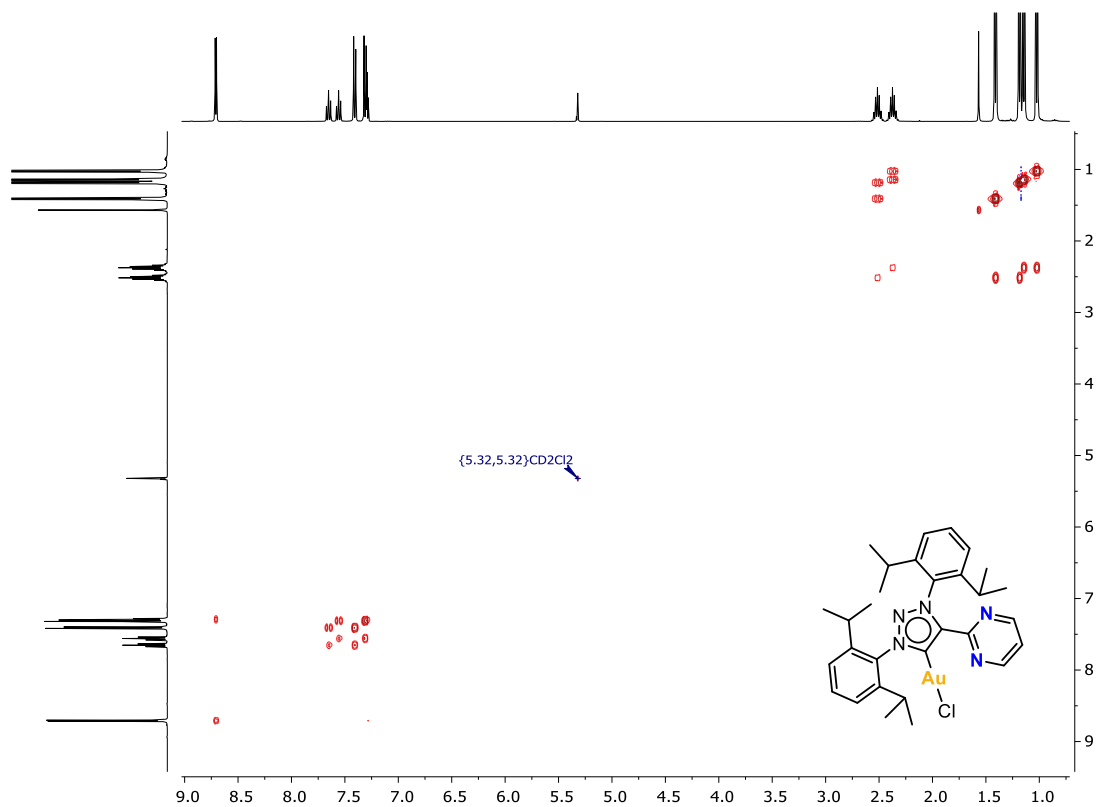


Figure S18.  $^1\text{H}$ ,  $^1\text{H}$ -COSY NMR (400MHz, 298K) of **2b** in  $\text{CD}_2\text{Cl}_2$ .

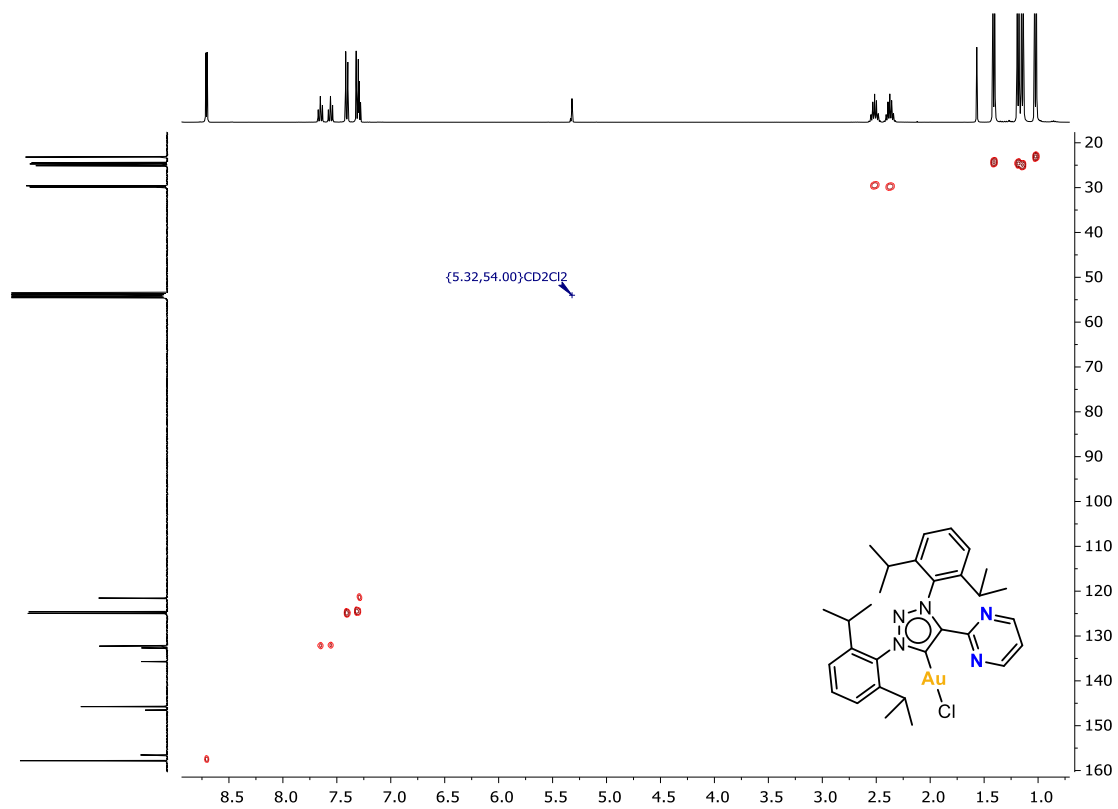
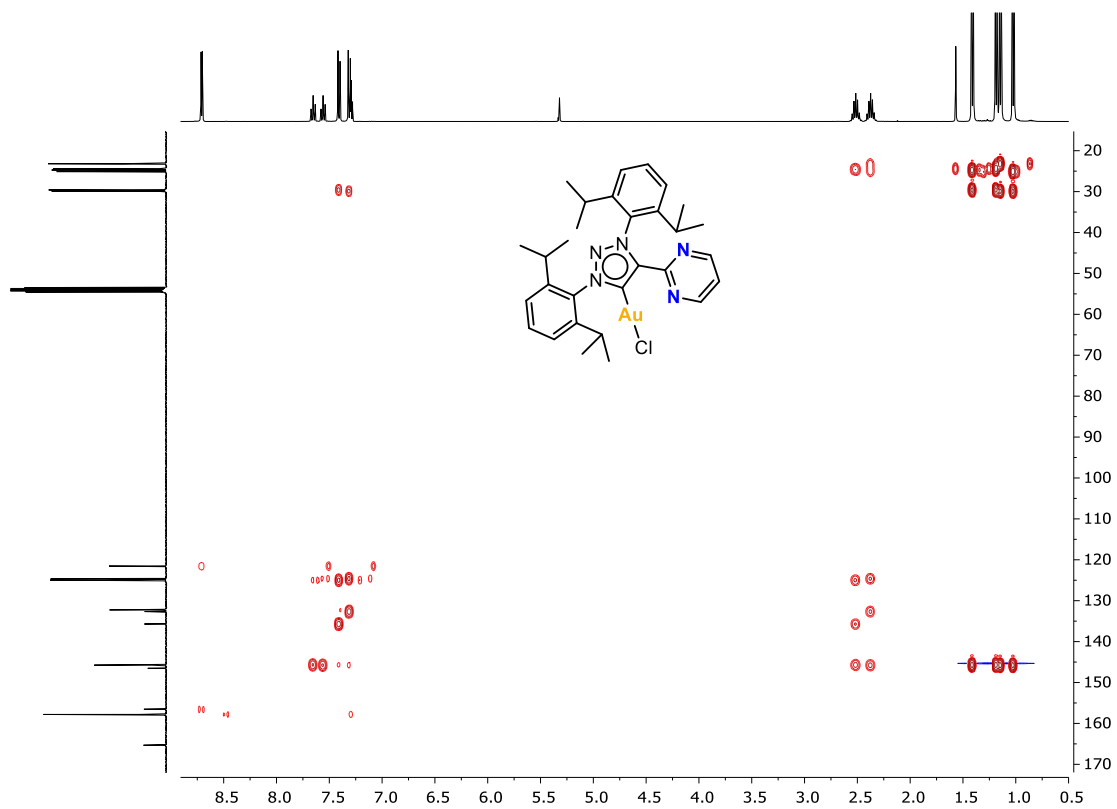


Figure S19.  $^1\text{H}$ ,  $^{13}\text{C}$ -HSQC NMR (400MHz, 298K) of **2b** in  $\text{CD}_2\text{Cl}_2$ .



**Figure S20.**  $^1\text{H}$ ,  $^{13}\text{C}$ -HMBC NMR (400MHz, 298K) of **2b** in  $\text{CD}_2\text{Cl}_2$ .

## 8.5 NMR Spectra of complex 3a

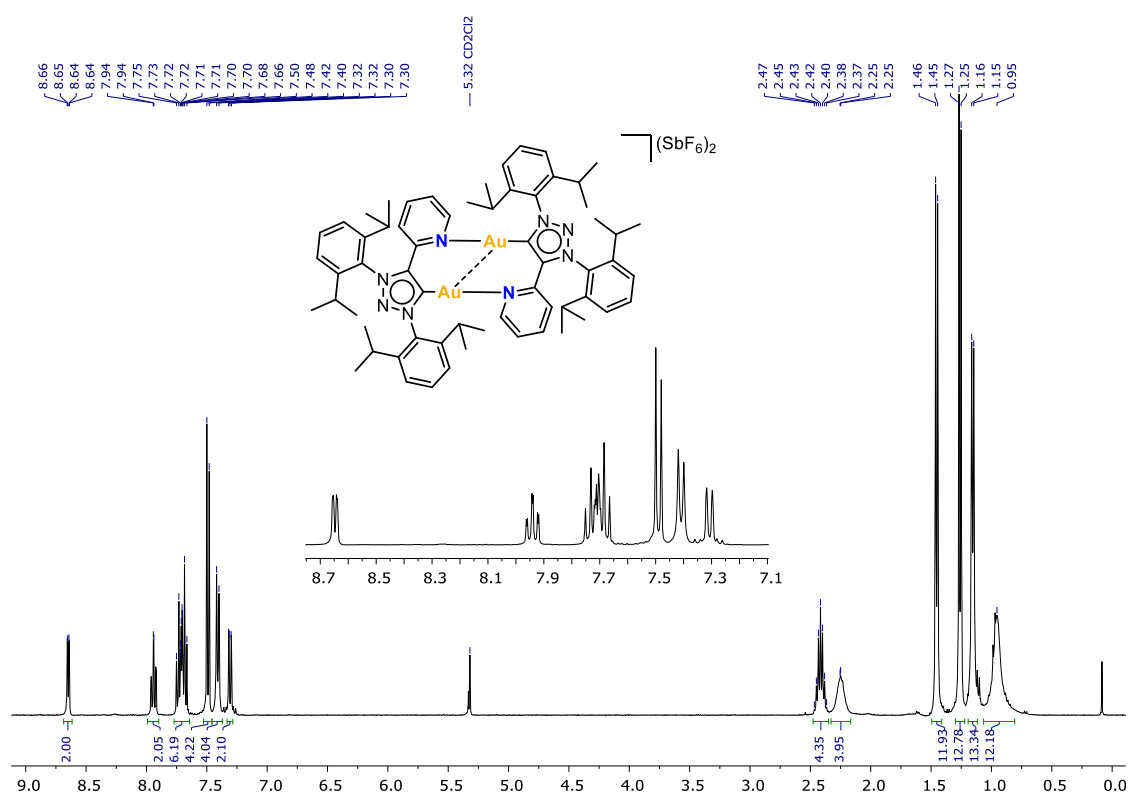


Figure S21. <sup>1</sup>H NMR (400MHz, 298K) of **3a** in CD<sub>2</sub>Cl<sub>2</sub>.

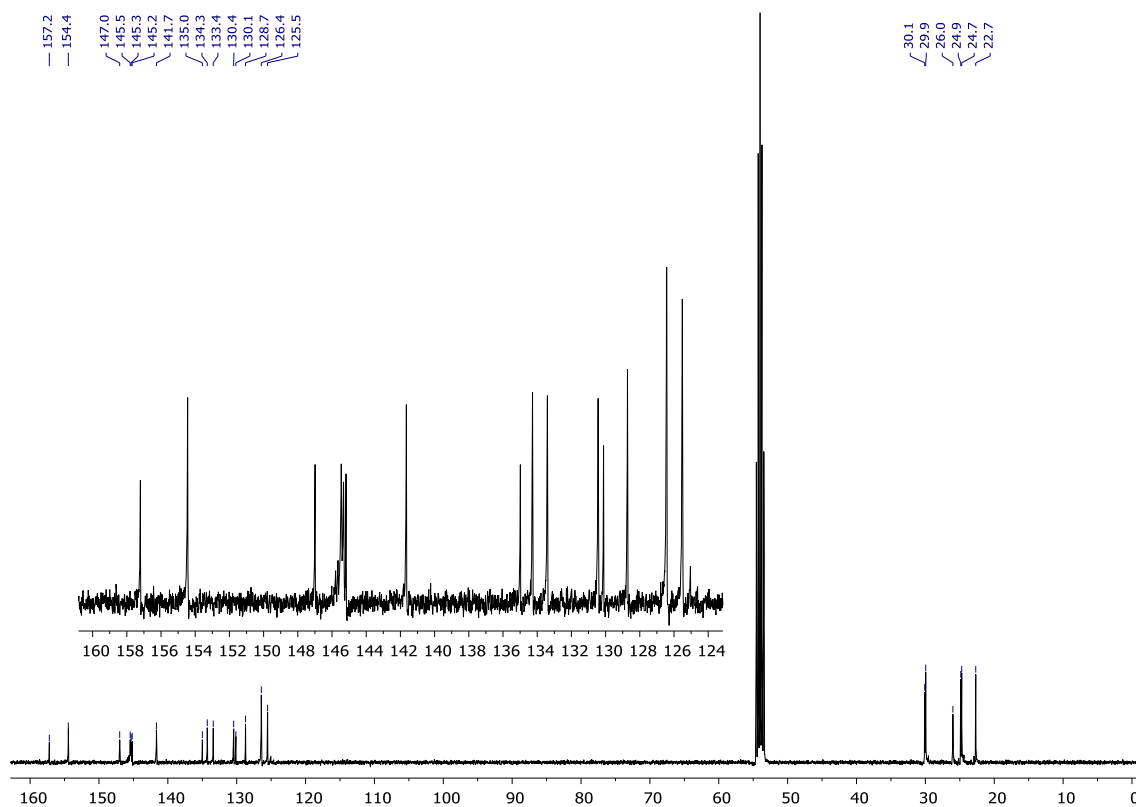


Figure S22. <sup>13</sup>C NMR (101MHz, 298K) of **3a** in CD<sub>2</sub>Cl<sub>2</sub>.



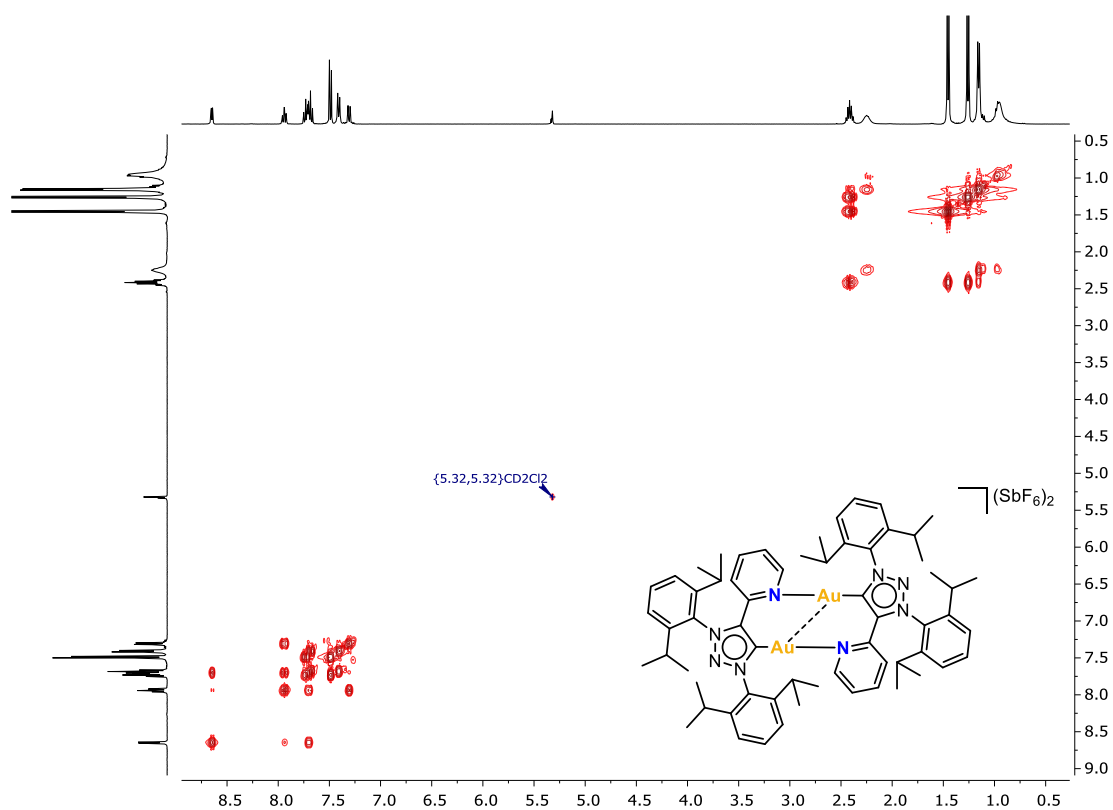


Figure S23.  $^1\text{H}, ^1\text{H}$ -COSY NMR (400MHz, 298K) of **3a** in  $\text{CD}_2\text{Cl}_2$ .

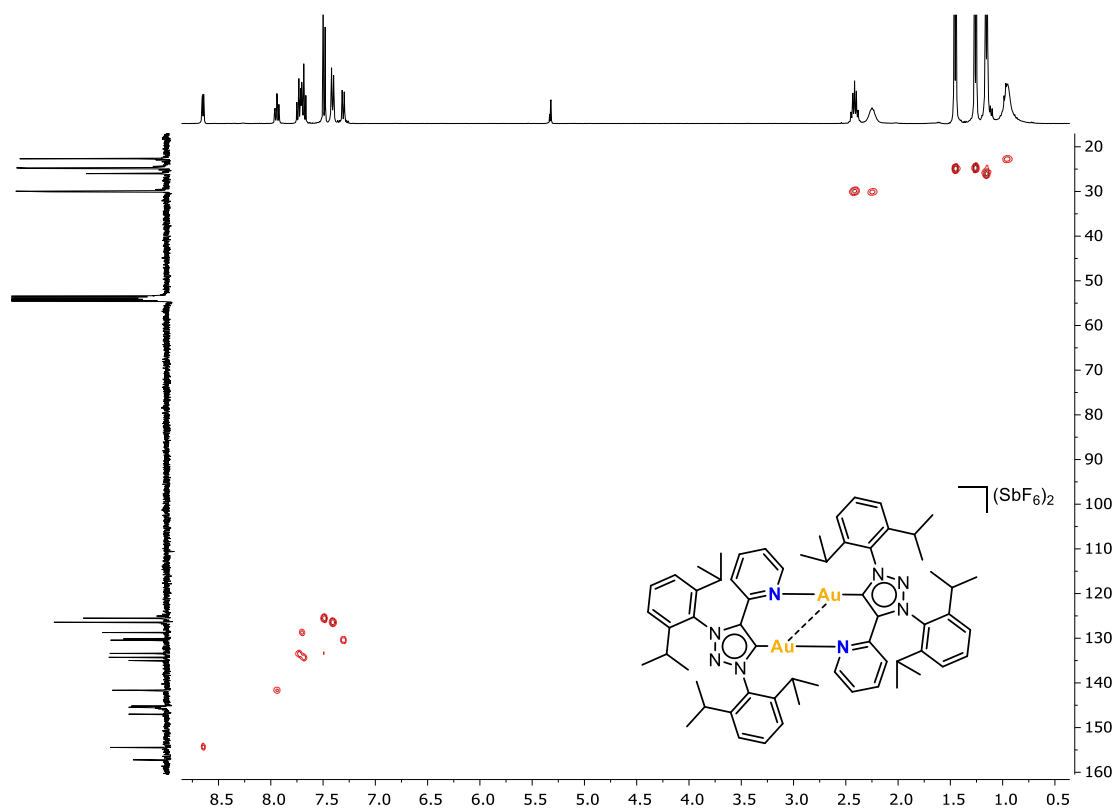
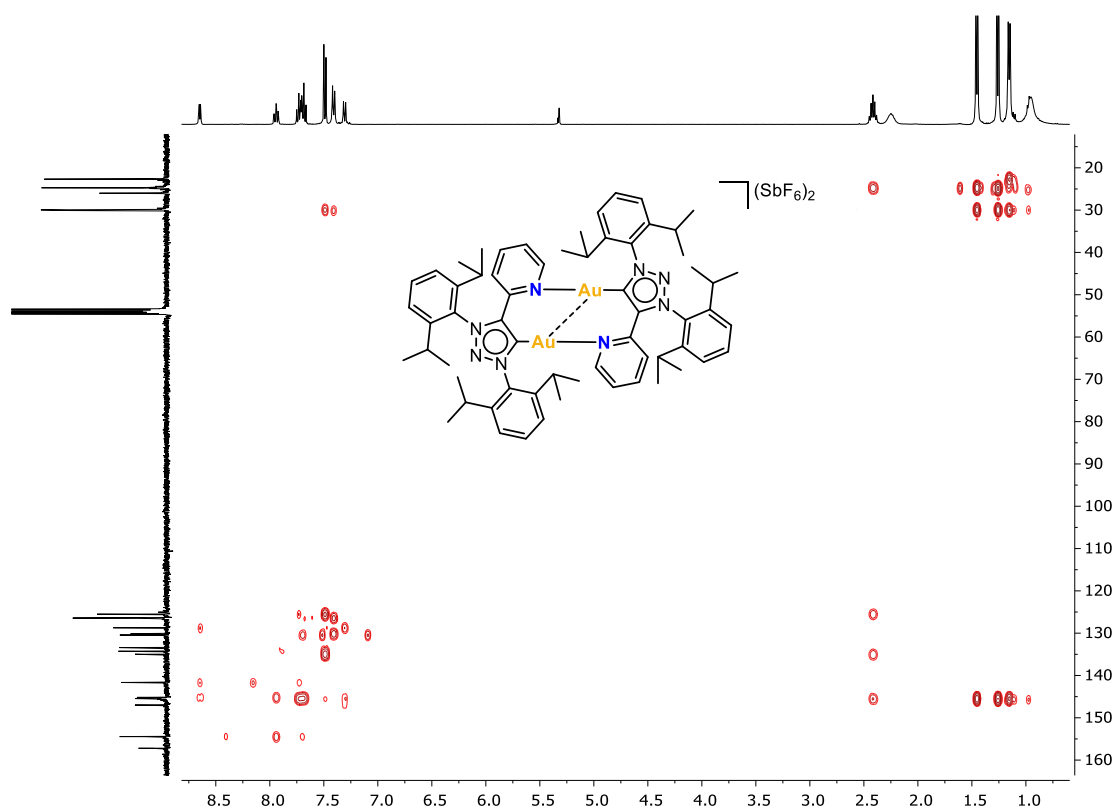


Figure S24.  $^1\text{H}, ^{13}\text{C}$ -HSQC NMR (400MHz, 298K) of **3a** in  $\text{CD}_2\text{Cl}_2$ .



**Figure S25.**  $^1\text{H}$ ,  $^{13}\text{C}$ -HMBC NMR (400MHz, 298K) of **3a** in  $\text{CD}_2\text{Cl}_2$ .

## 8.6 NMR Spectra of complex 3b

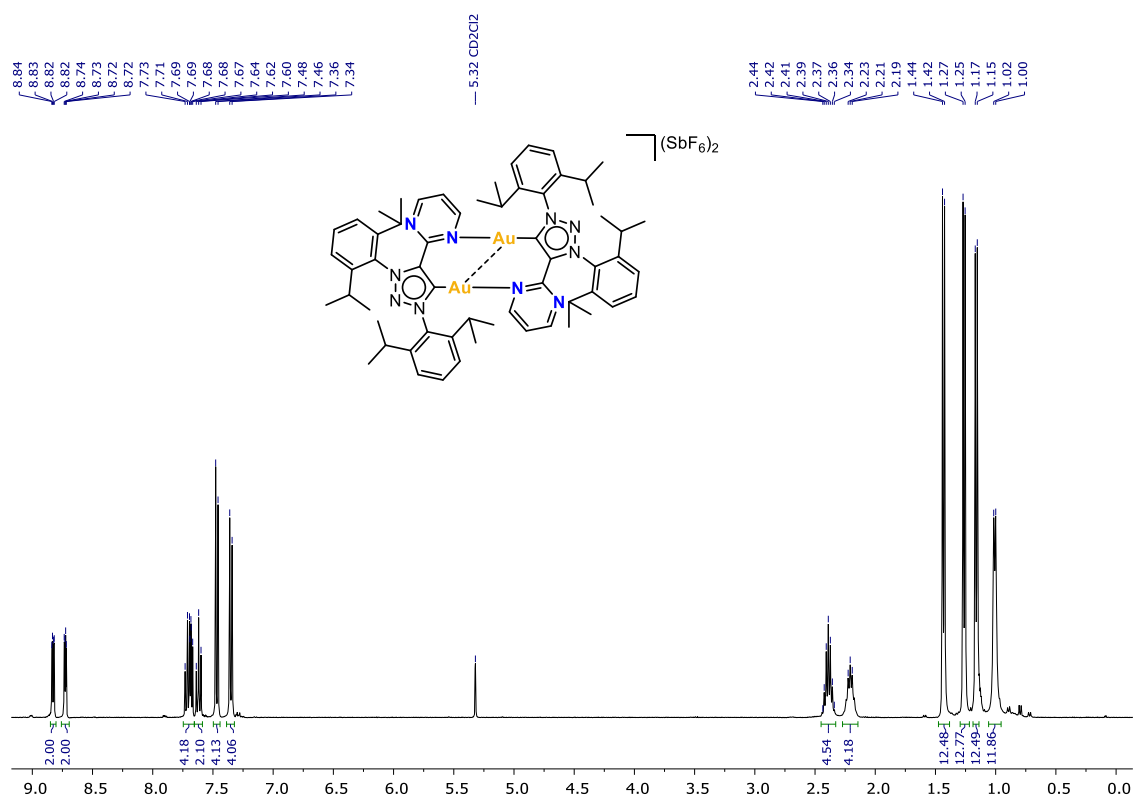


Figure S26.  $^1\text{H}$  NMR (400MHz, 298K) of **3b** in  $\text{CD}_2\text{Cl}_2$ .

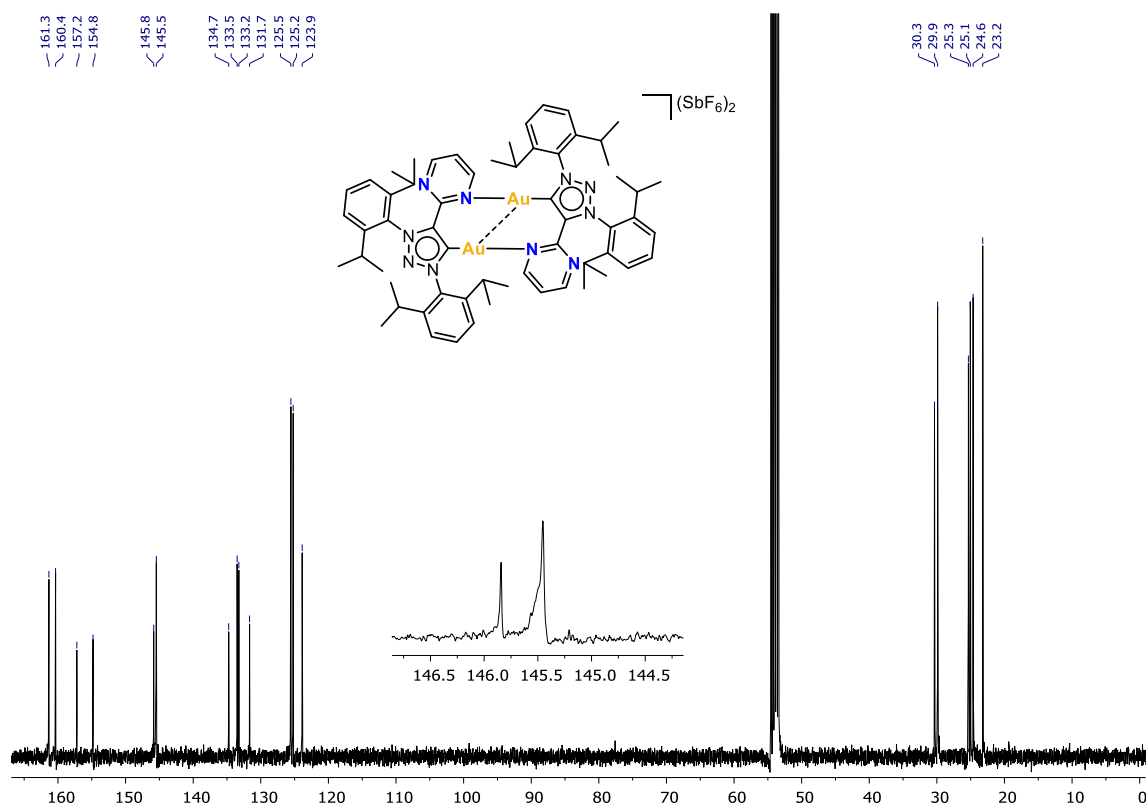


Figure S27.  $^{13}\text{C}$  NMR (101MHz, 298K) of **3b** in  $\text{CD}_2\text{Cl}_2$ .

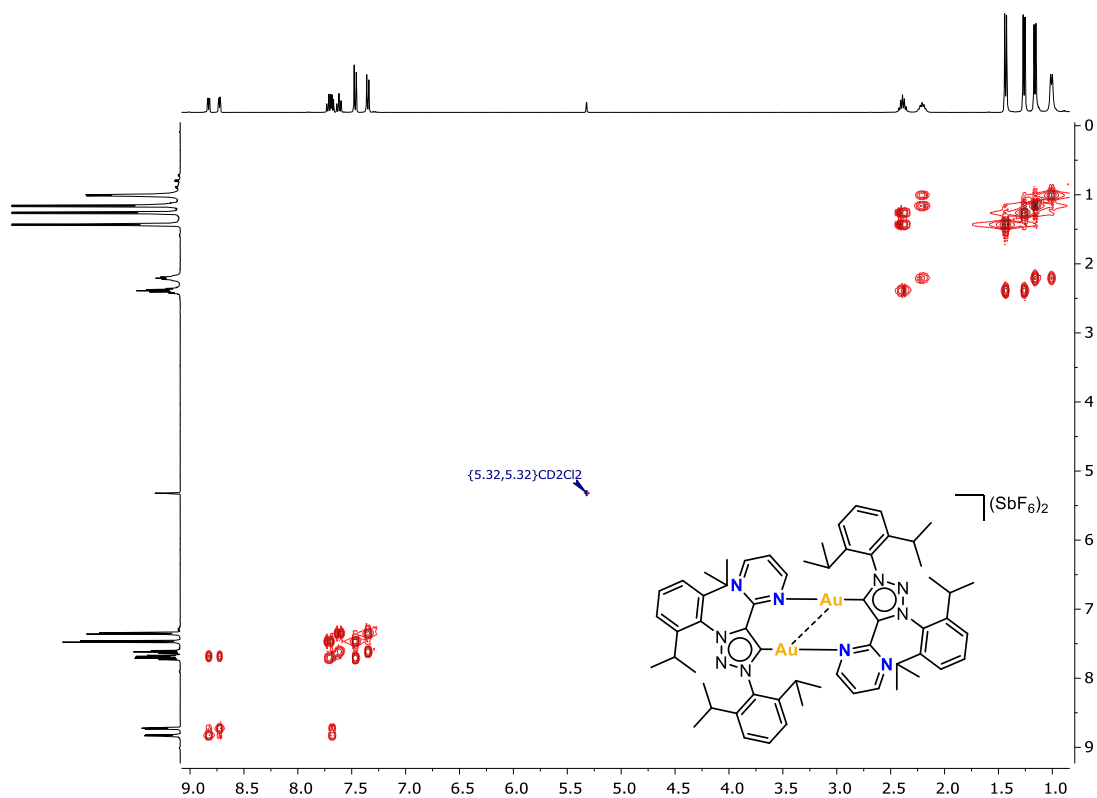


Figure S28.  $^1\text{H}, ^1\text{H}$ -COSY NMR (400MHz, 298K) of **3b** in  $\text{CD}_2\text{Cl}_2$ .

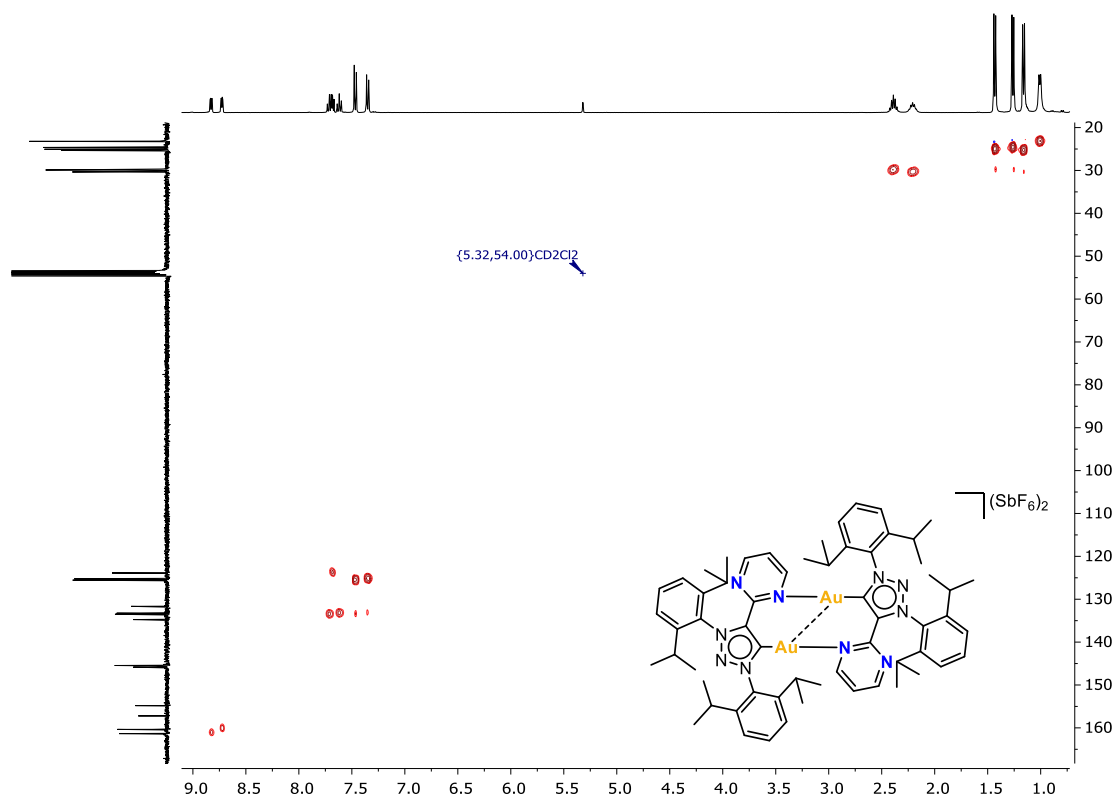
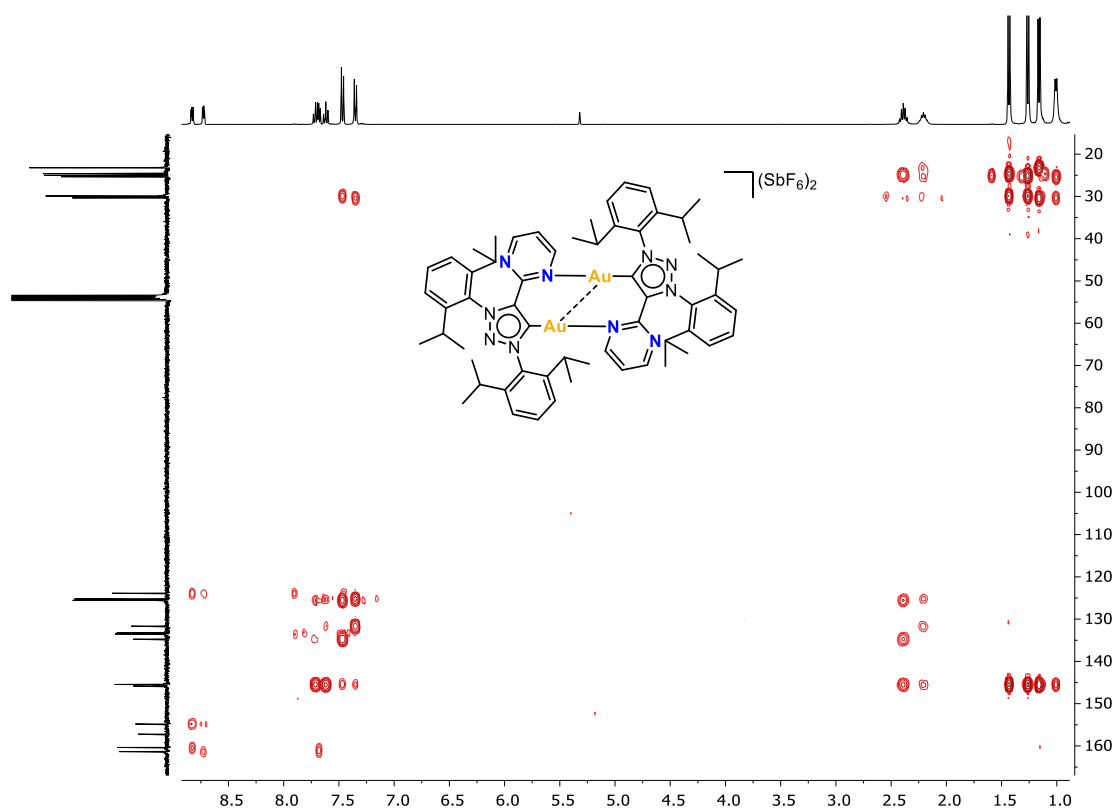


Figure S29.  $^1\text{H}, ^{13}\text{C}$ -HSQC NMR (400MHz, 298K) of **3b** in  $\text{CD}_2\text{Cl}_2$ .



**Figure S30.**  $^1\text{H}$ ,  $^{13}\text{C}$ -HMBC NMR (400MHz, 298K) of **3b** in  $\text{CD}_2\text{Cl}_2$ .

## 8.7 NMR and HRMS-ESI Spectra of complex 4a-Cl

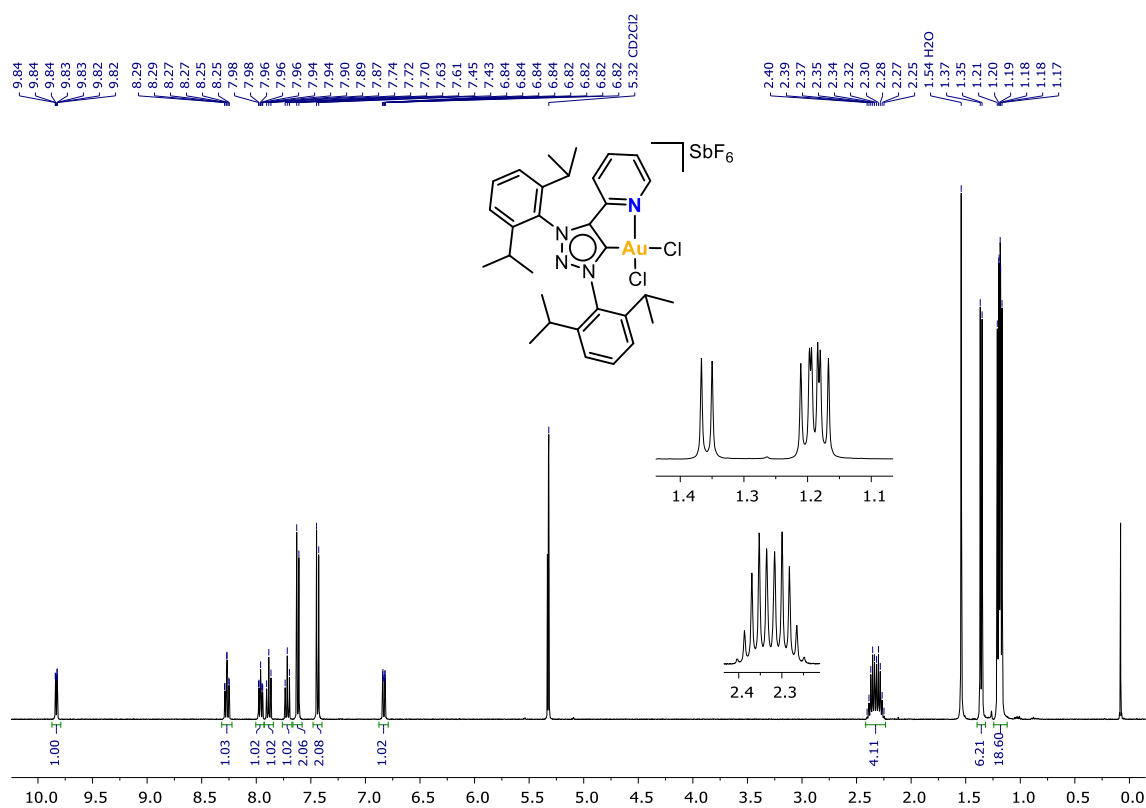


Figure S31.  $^1\text{H NMR}$  (400MHz, 298K) of 4a-Cl in  $\text{CD}_2\text{Cl}_2$ .

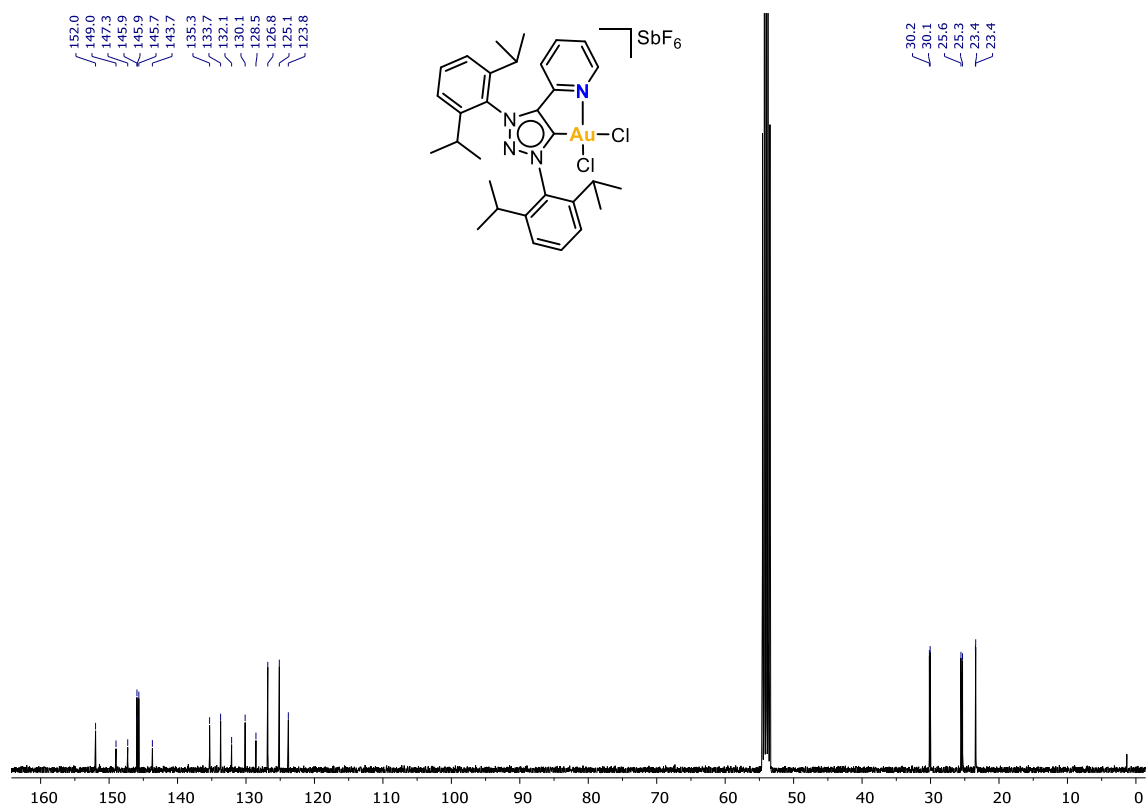


Figure S32.  $^{13}\text{C NMR}$  (101MHz, 298K) of 4a-Cl in  $\text{CD}_2\text{Cl}_2$ .

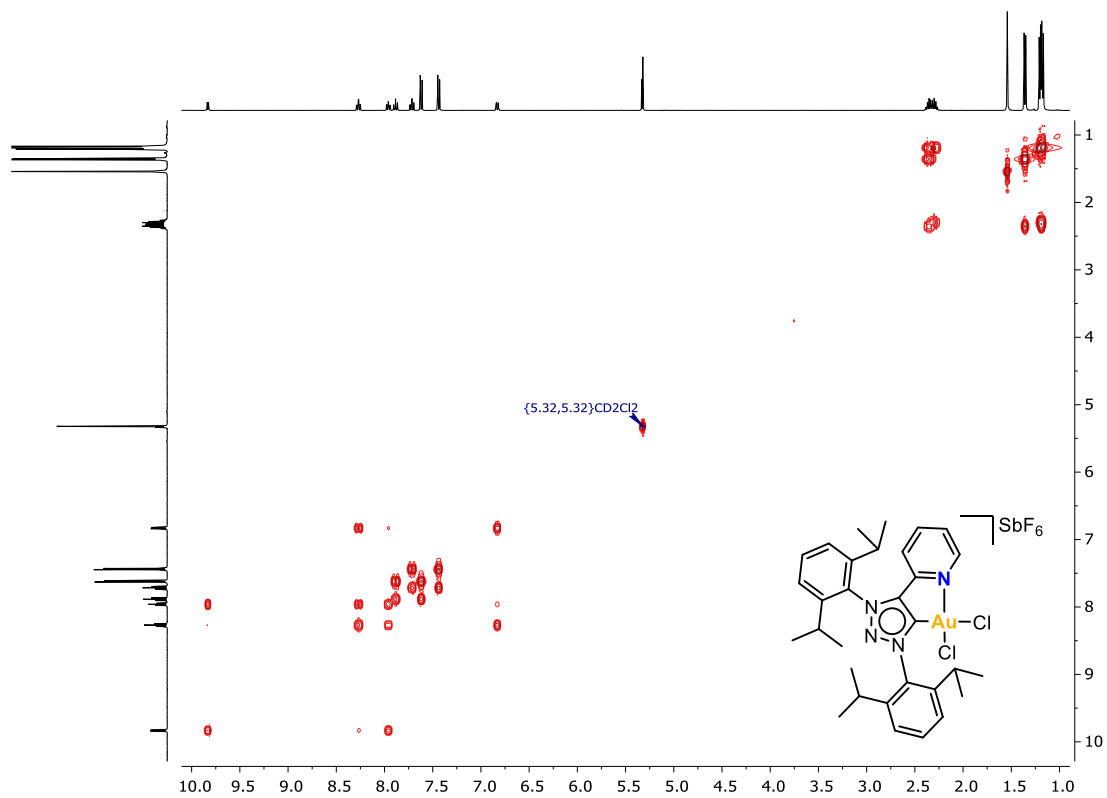


Figure S33.  $^1\text{H}$ ,  $^1\text{H}$ -COSY NMR (400MHz, 298K) of **4a-Cl** in  $\text{CD}_2\text{Cl}_2$ .

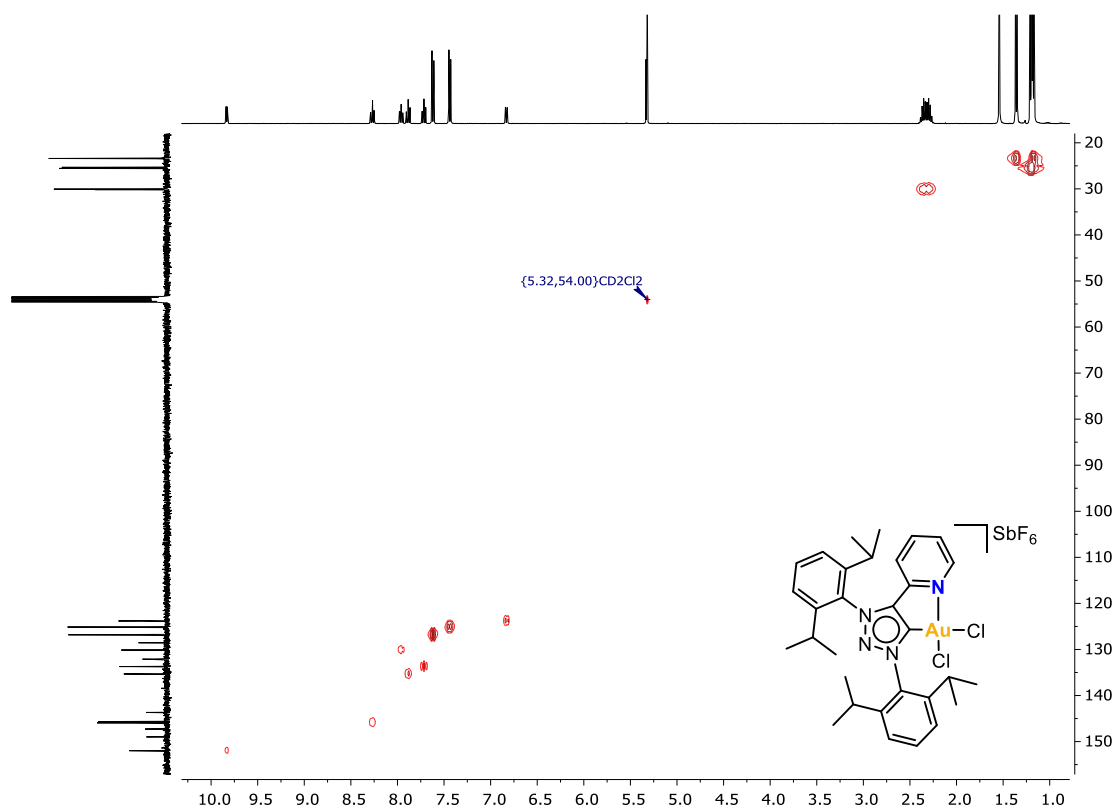


Figure S34.  $^1\text{H}$ ,  $^{13}\text{C}$ -HSQC NMR (400MHz, 298K) of **4a-Cl** in  $\text{CD}_2\text{Cl}_2$ .

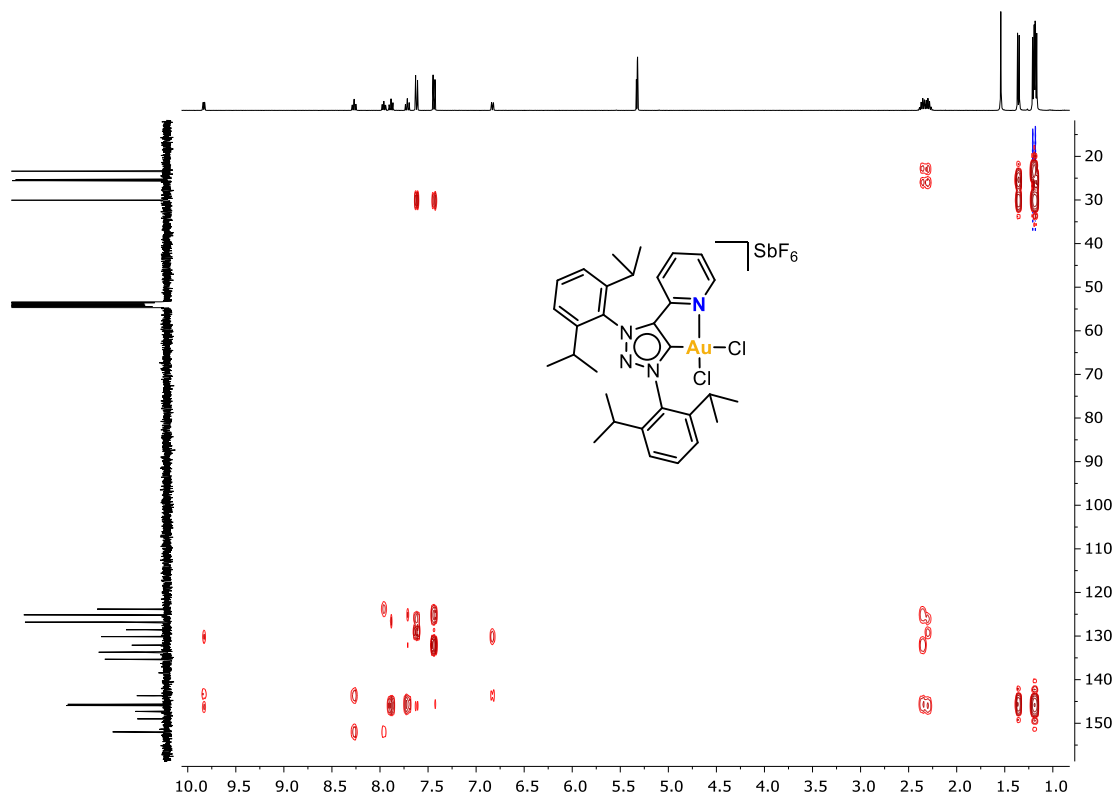


Figure S35.  $^1\text{H}$ ,  $^{13}\text{C}$ -HMBC NMR (400MHz, 298K) of **4a-Cl** in  $\text{CD}_2\text{Cl}_2$ .

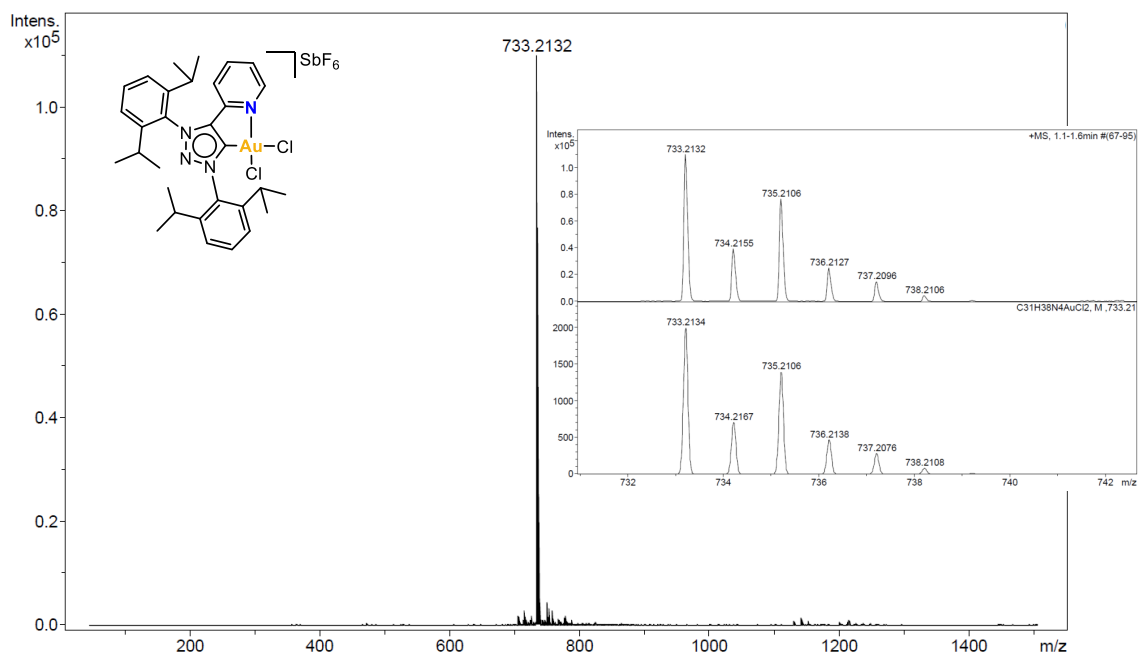


Figure S36. HRMS-ESI(+) of **4a-Cl**.



## 8.8 NMR and HRMS-ESI Spectra of complex 4a-OAc

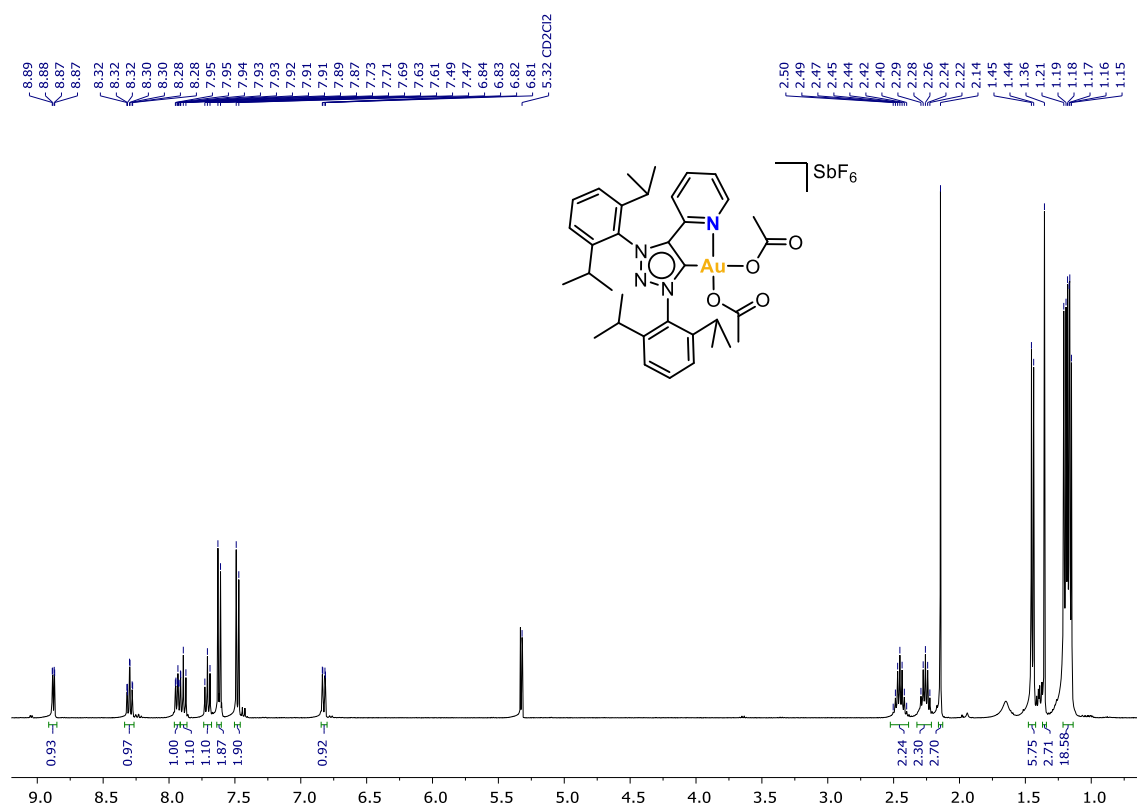


Figure S37. <sup>1</sup>H NMR (400MHz, 298K) of 4a-OAc in CD<sub>2</sub>Cl<sub>2</sub>.

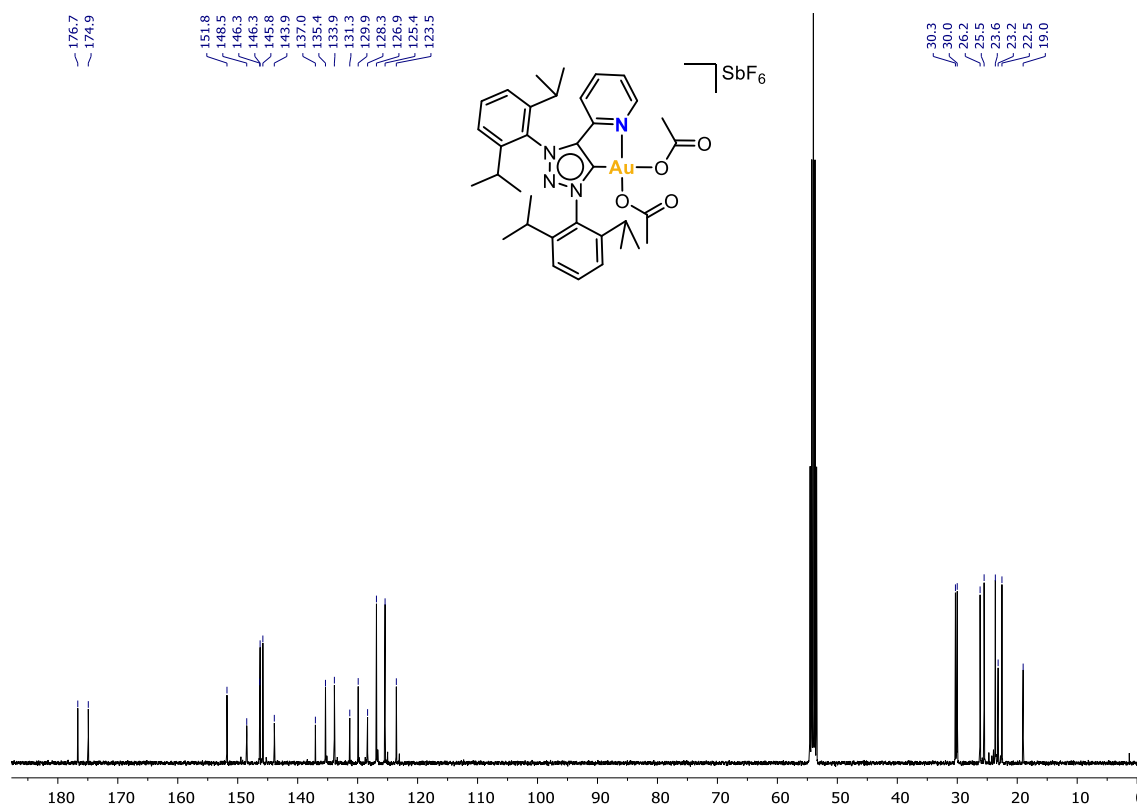


Figure S38. <sup>13</sup>C NMR (101MHz, 298K) of 4a-OAc in CD<sub>2</sub>Cl<sub>2</sub>.

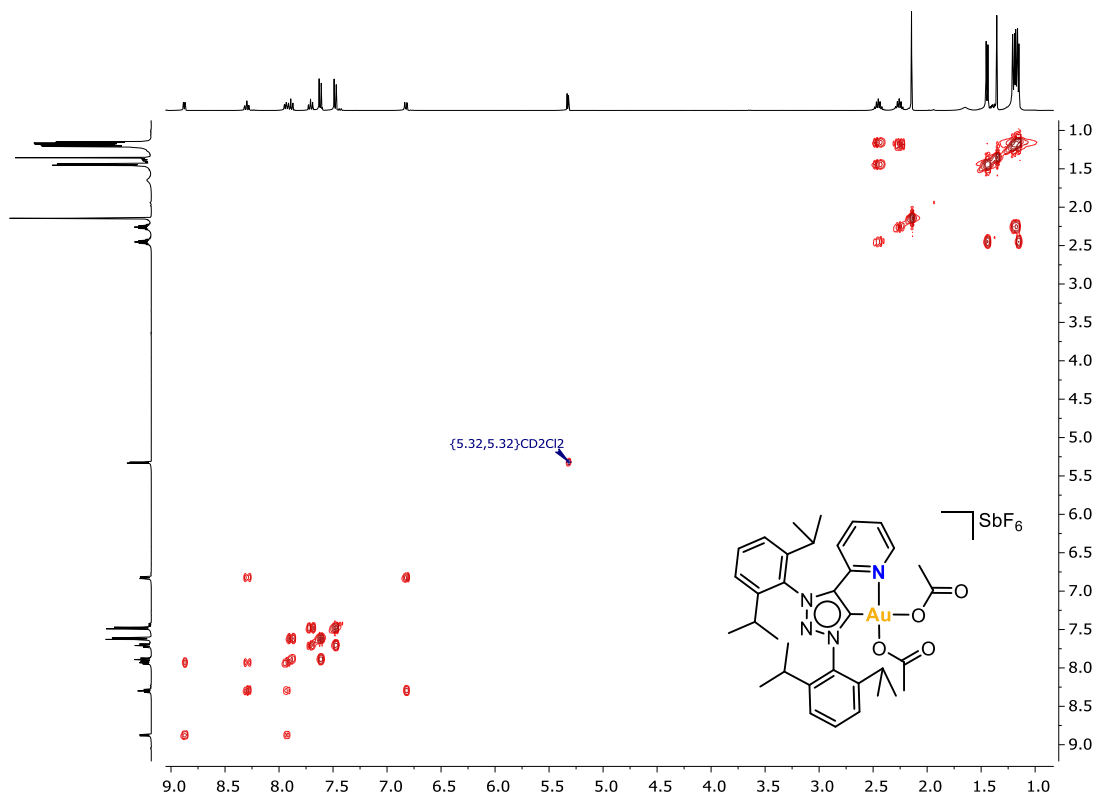


Figure S39.  $^1\text{H}$ ,  $^1\text{H}$ -COSY NMR (400MHz, 298K) of **4a-OAc** in  $\text{CD}_2\text{Cl}_2$ .

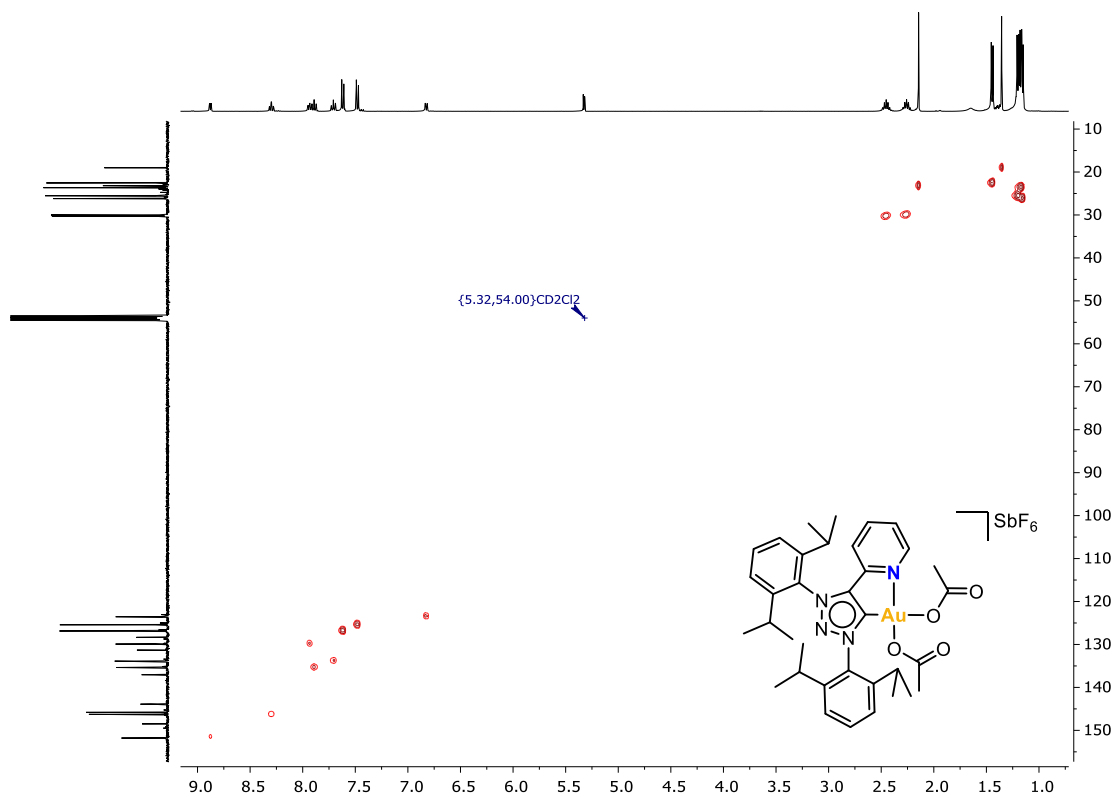


Figure S40.  $^1\text{H}$ ,  $^{13}\text{C}$ -HSQC NMR (400MHz, 298K) of **4a-OAc** in  $\text{CD}_2\text{Cl}_2$ .

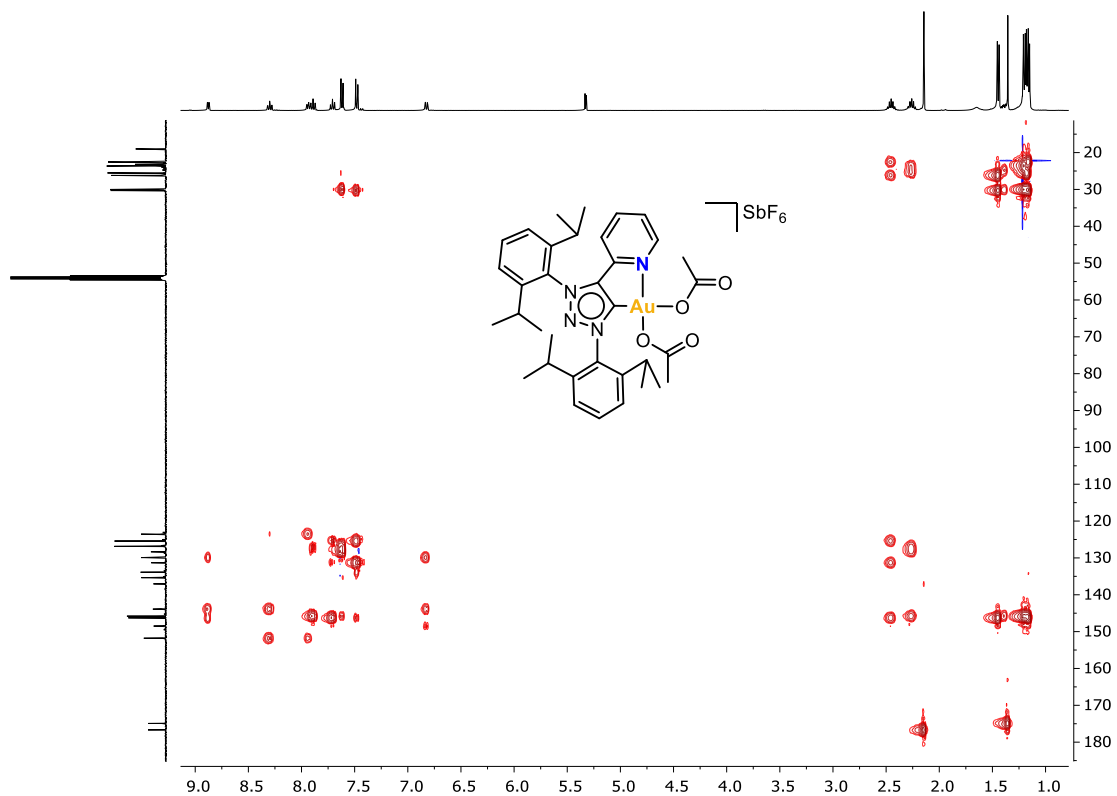


Figure S41.  $^1\text{H}$ ,  $^{13}\text{C}$ -HMBC NMR (400MHz, 298K) of **4a-OAc** in  $\text{CD}_2\text{Cl}_2$ .

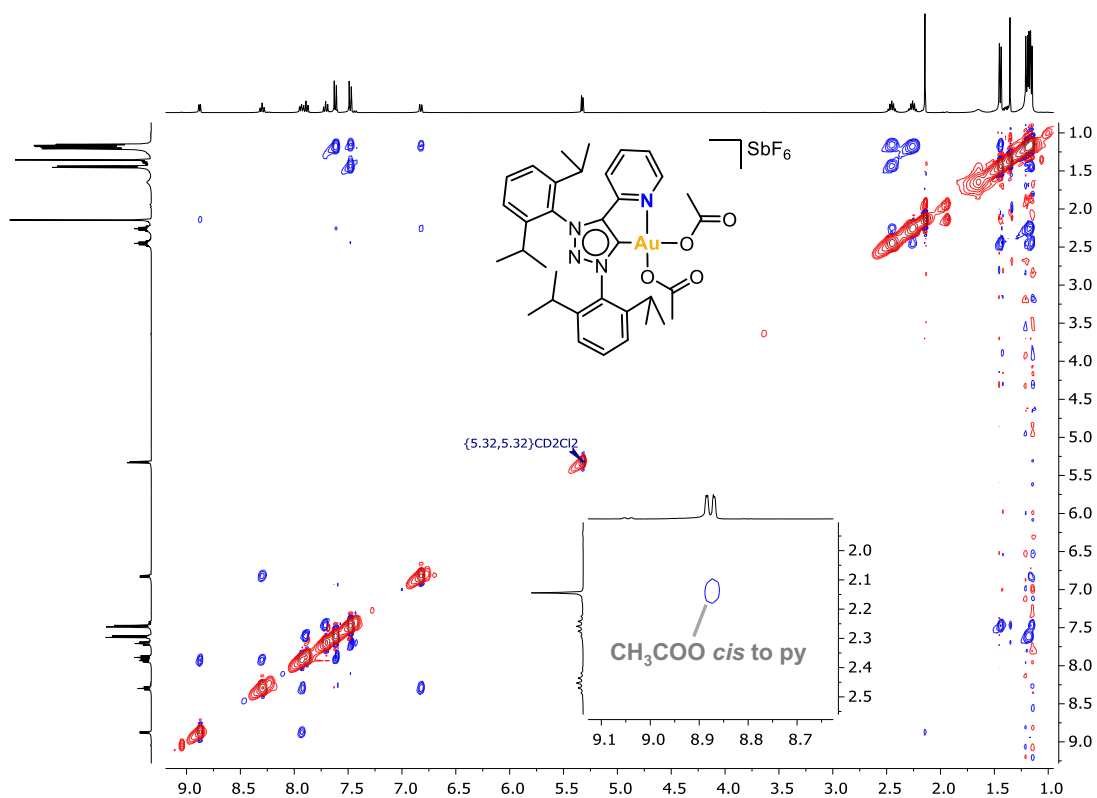
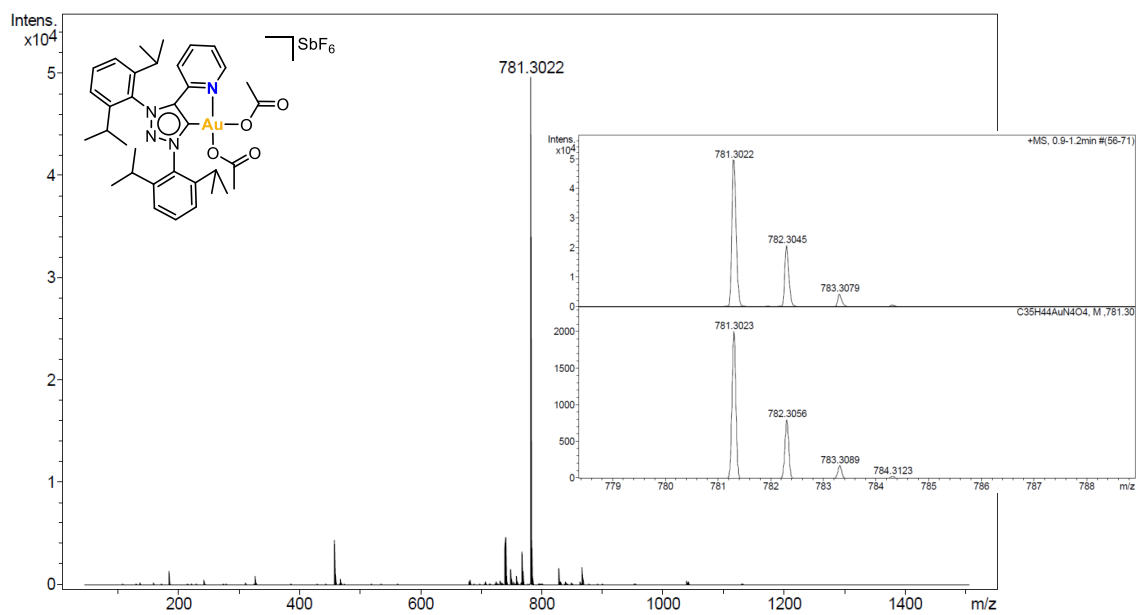
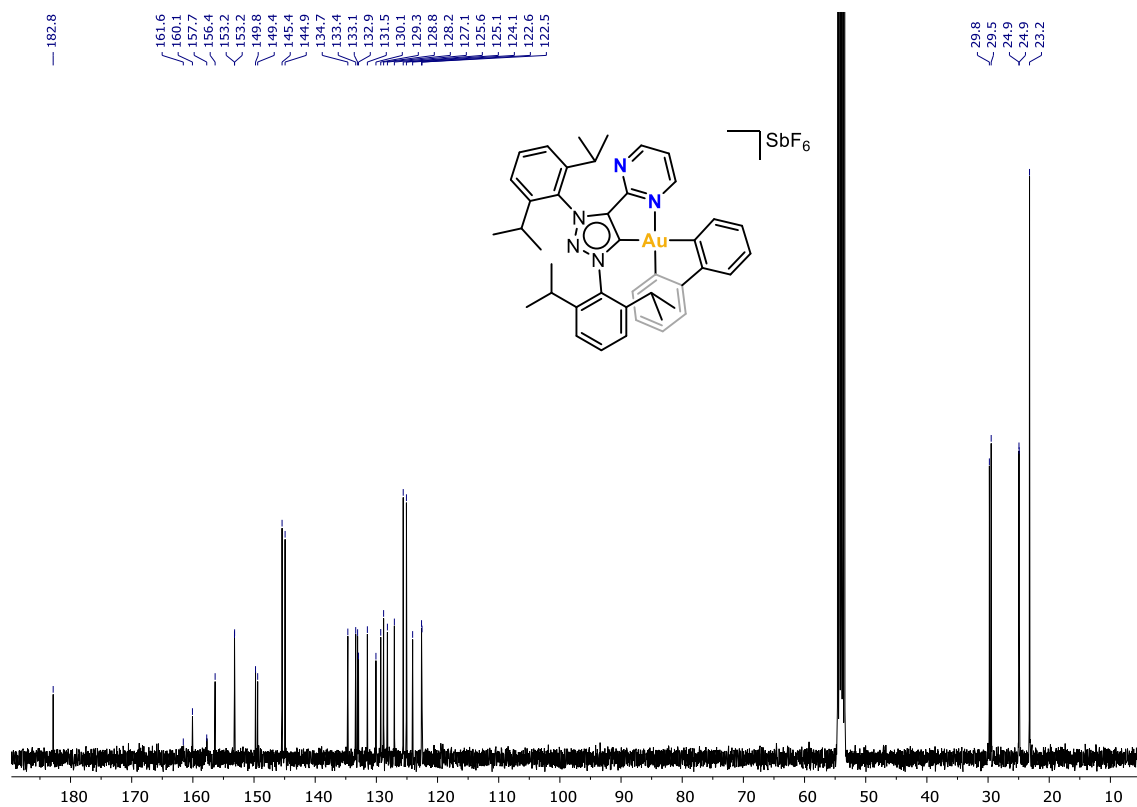
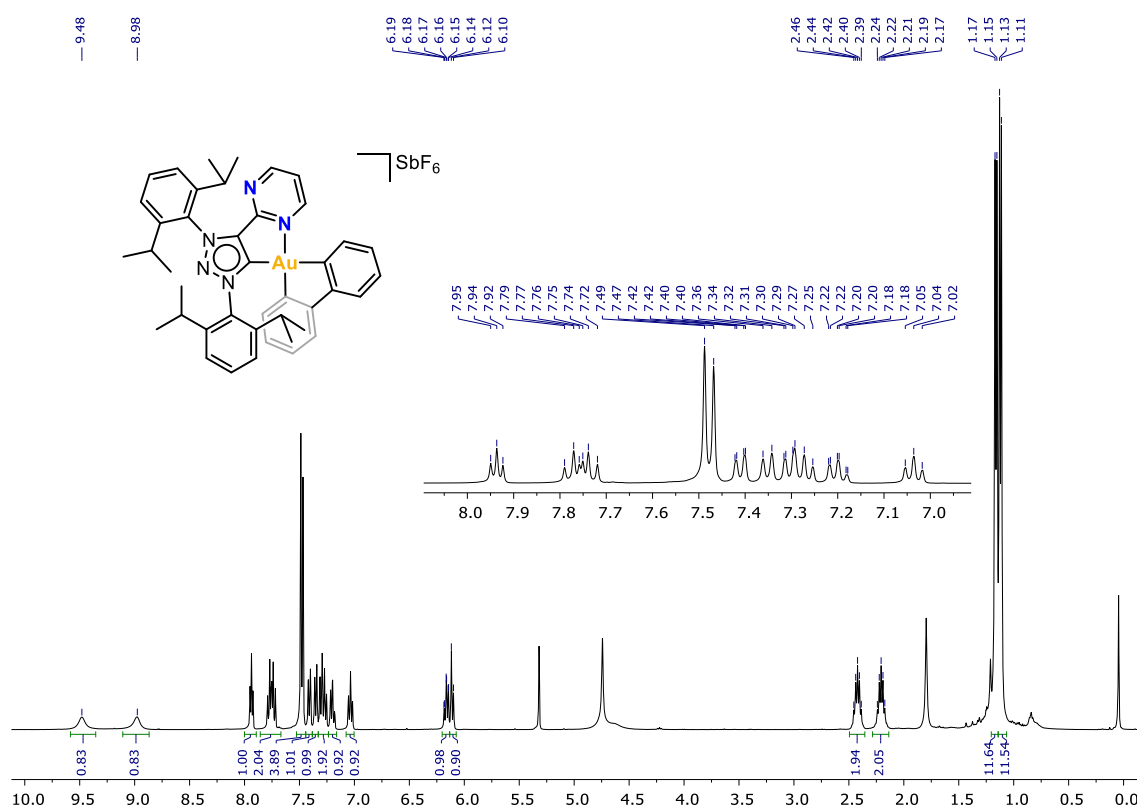


Figure S42.  $^1\text{H}$ ,  $^1\text{H}$ -NOESY NMR (400MHz, 298K) of **4a-OAc** in  $\text{CD}_2\text{Cl}_2$ .



**Figure S43.** HRMS-ESI(+) of **4a-OAc**.

## 8.9 NMR and HRMS-ESI Spectra of complex **5b**



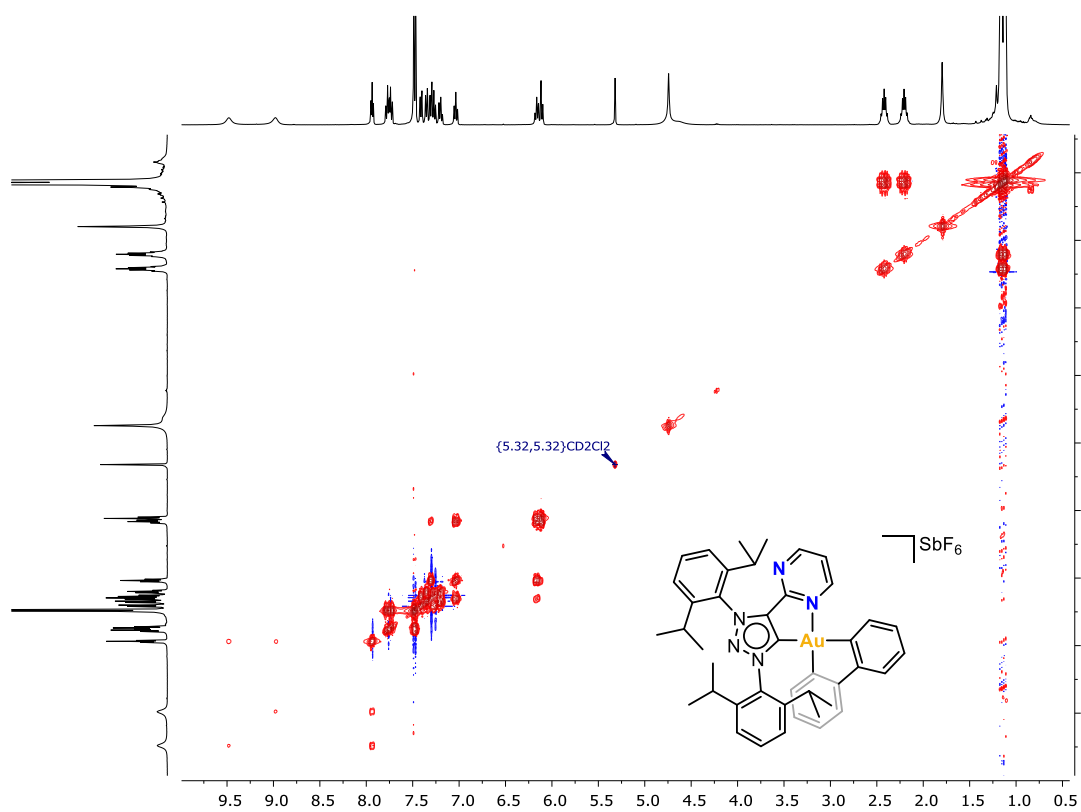


Figure S46.  $^1\text{H}$ ,  $^1\text{H}$ -COSY NMR (400MHz, 248K) of **5b** in  $\text{CD}_2\text{Cl}_2$ .

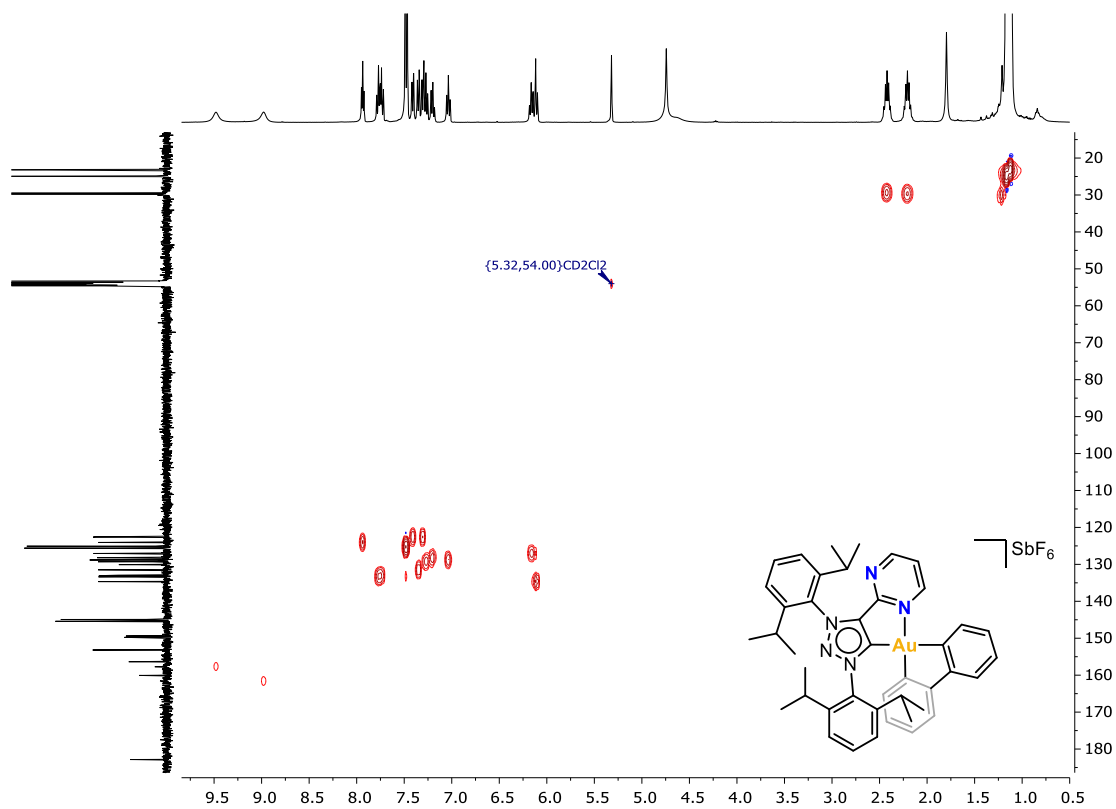


Figure S47.  $^1\text{H}$ ,  $^{13}\text{C}$ -HSQC NMR (400MHz, 248K) of **5b** in  $\text{CD}_2\text{Cl}_2$ .

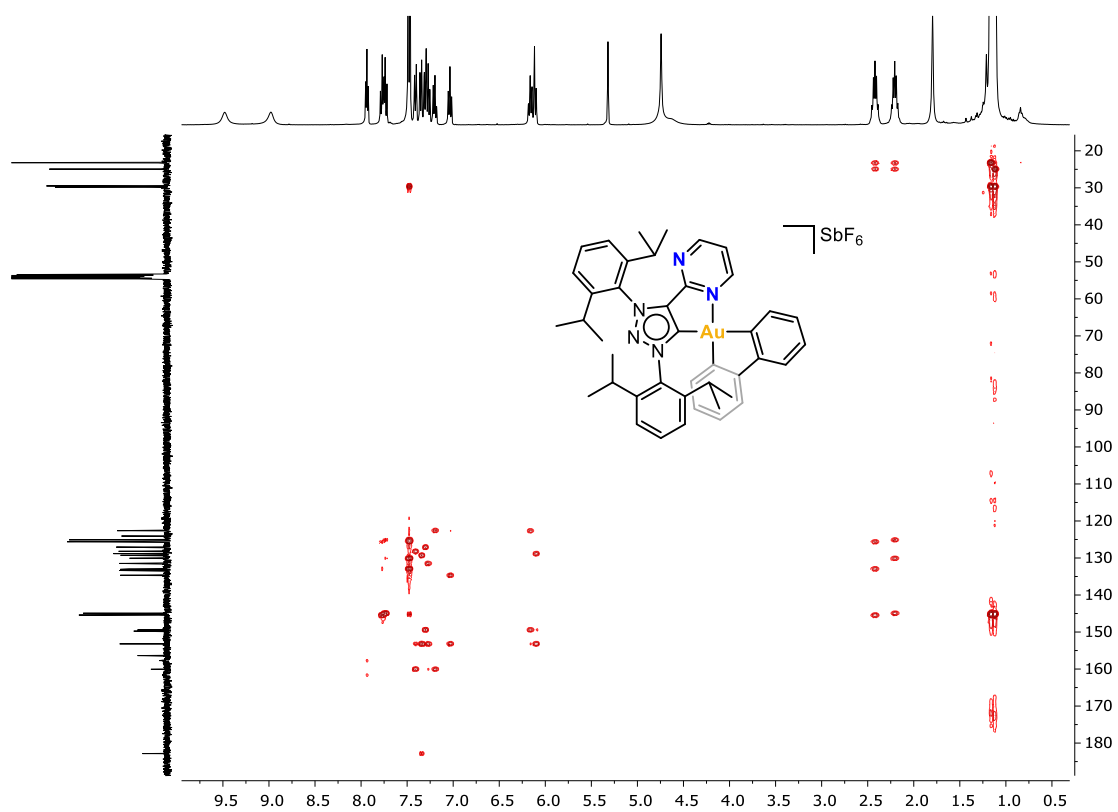


Figure S48.  $^1\text{H}$ ,  $^{13}\text{C}$ -HMBC NMR (400MHz, 248K) of **5b** in  $\text{CD}_2\text{Cl}_2$ .

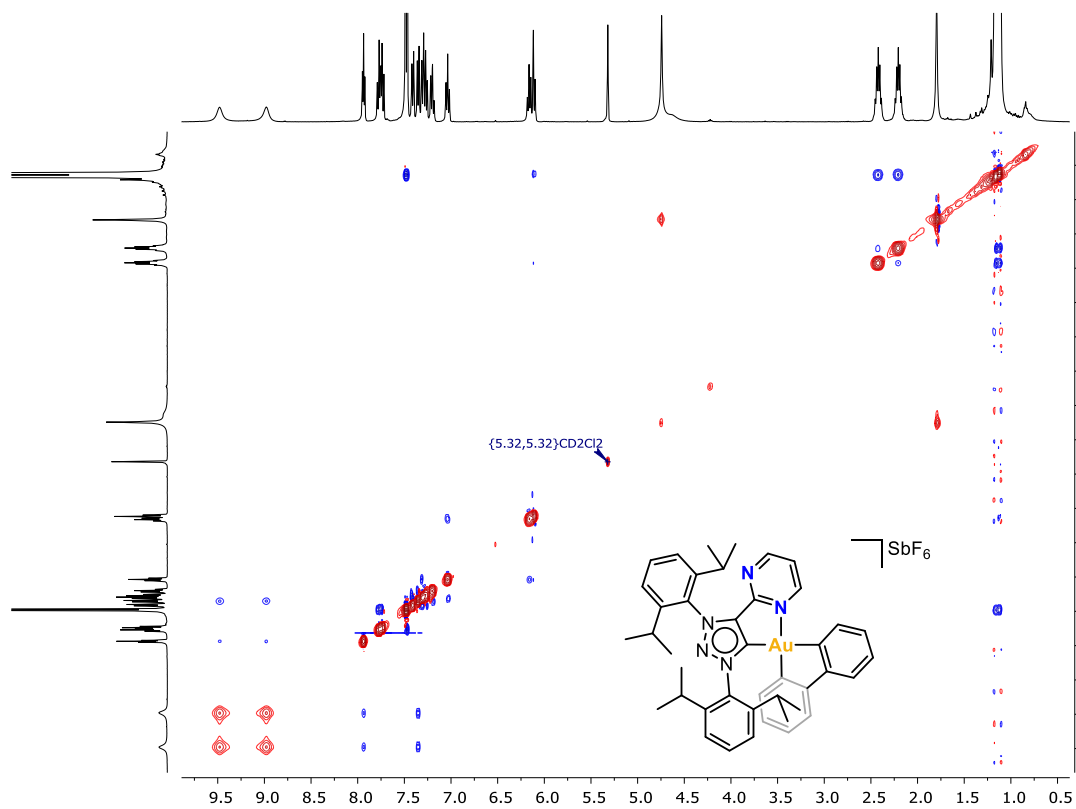
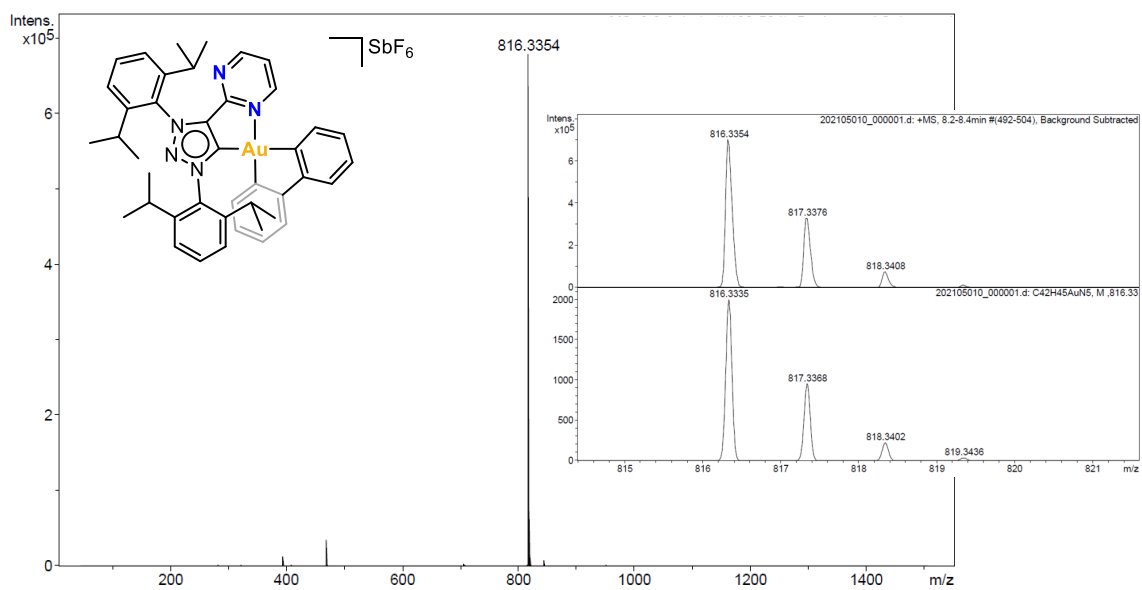


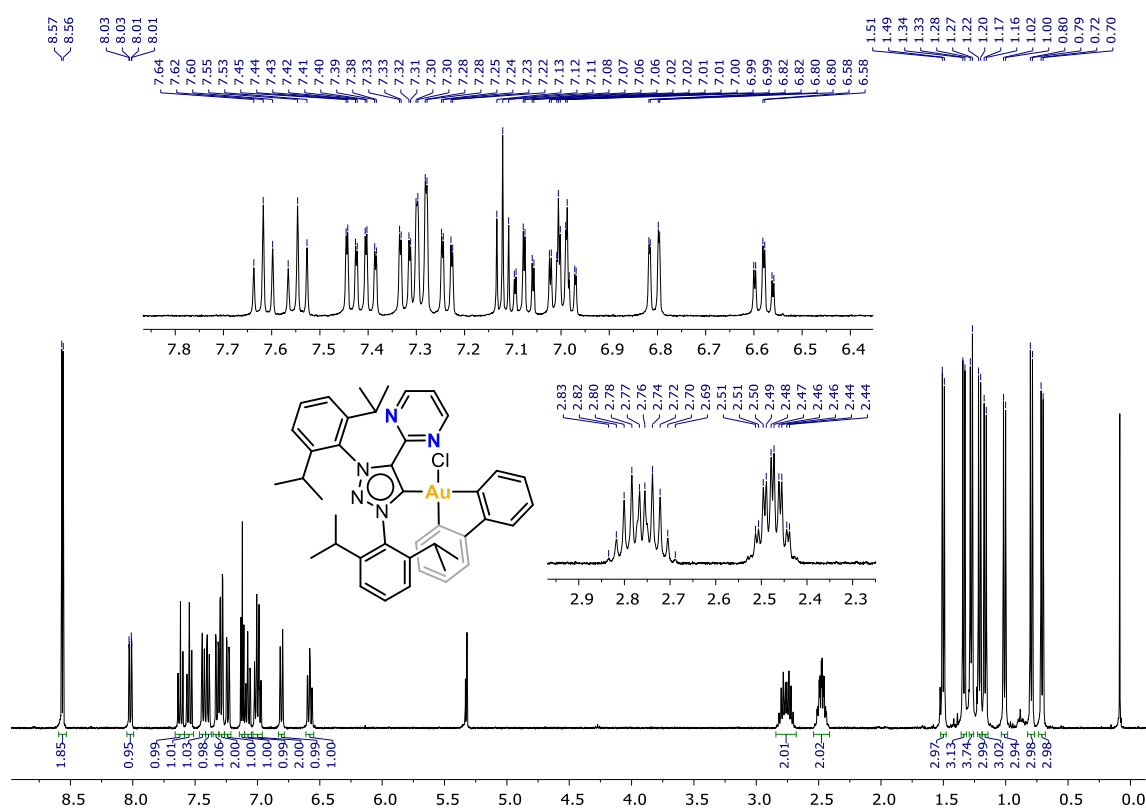
Figure S49.  $^1\text{H}$ ,  $^1\text{H}$ -NOESY NMR (400MHz, 248K) of **5b** in  $\text{CD}_2\text{Cl}_2$ .



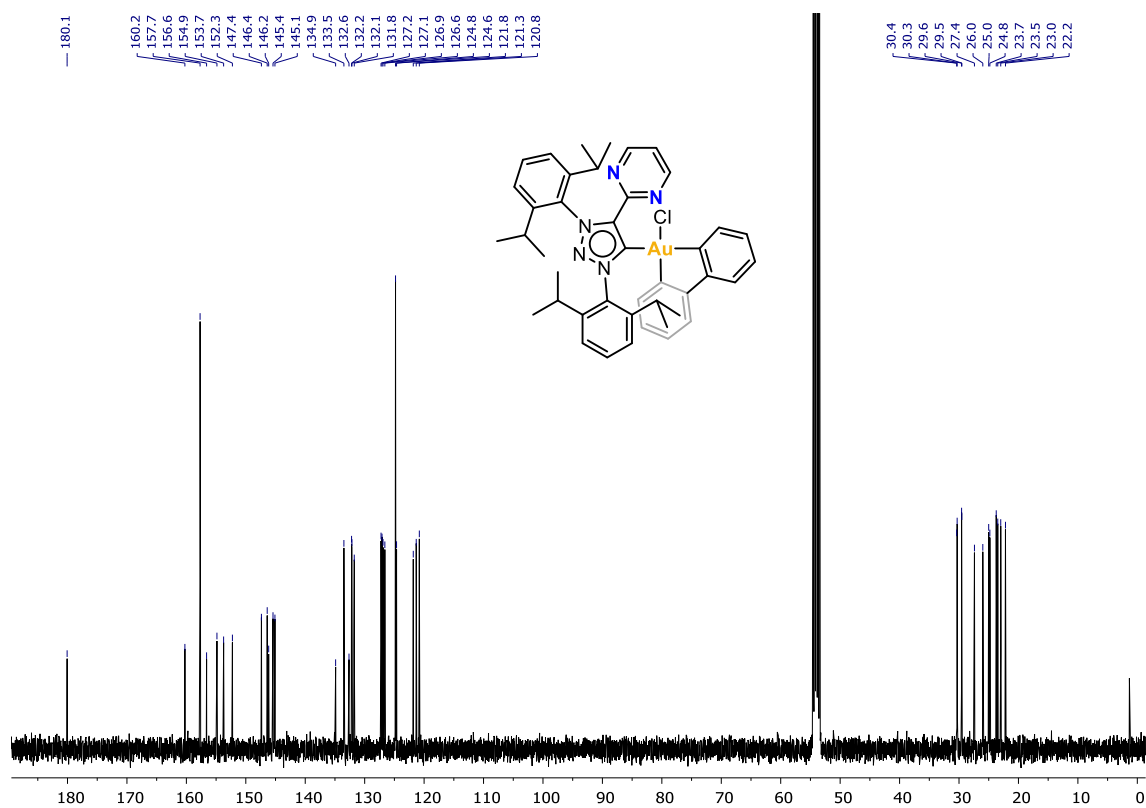
**Figure S50.** HRMS-ESI(+) of **5b**.



## 8.10 NMR and HRMS-ESI Spectra of complex **6b**



**Figure S51.**  $^1\text{H}$  NMR (400MHz, 298K) of **6b** in  $\text{CD}_2\text{Cl}_2$ .



**Figure S52.**  $^{13}\text{C}$  NMR (101MHz, 298K) of **6b** in  $\text{CD}_2\text{Cl}_2$ .

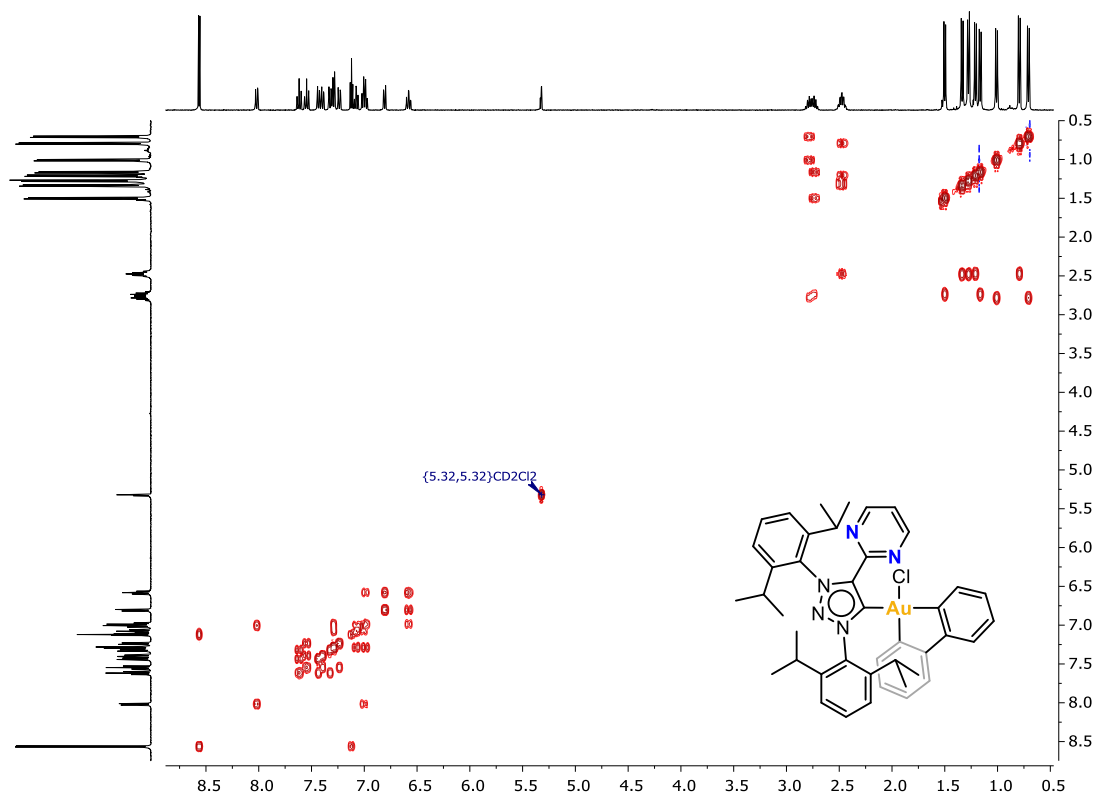


Figure S53.  $^1\text{H}$ ,  $^1\text{H}$ -COSY NMR (400MHz, 298K) of **6b** in  $\text{CD}_2\text{Cl}_2$ .

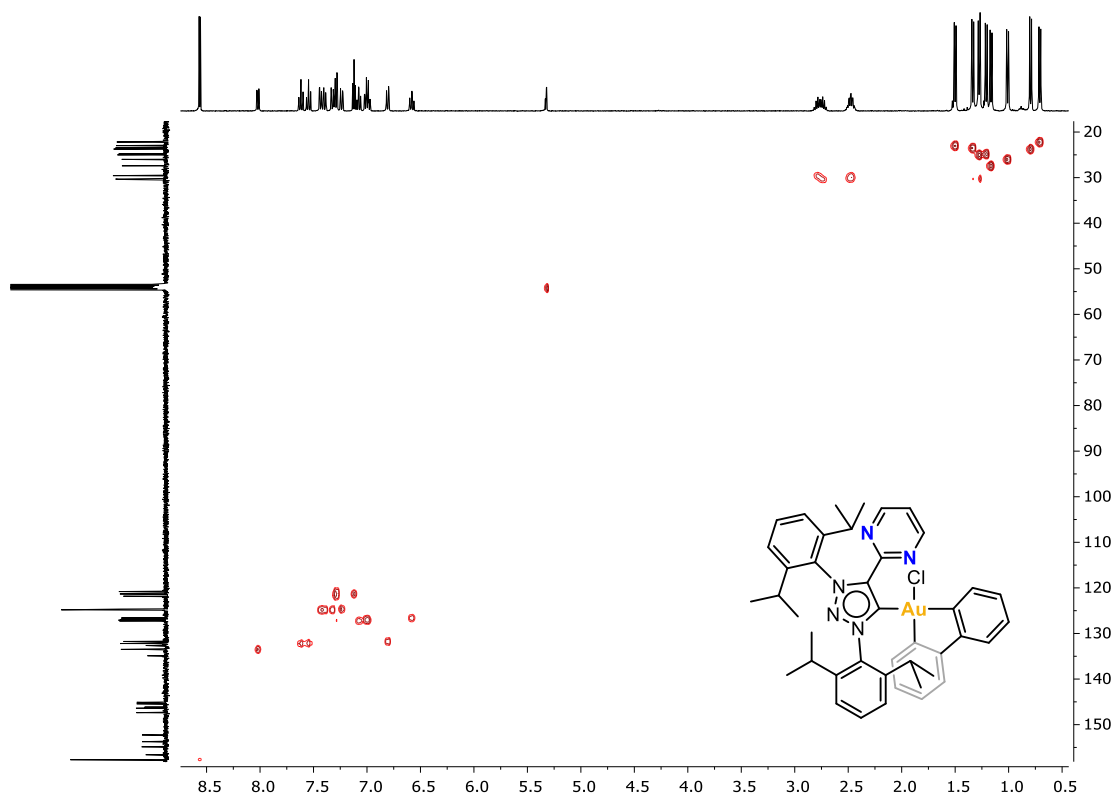


Figure S54.  $^1\text{H}$ ,  $^{13}\text{C}$ -HSQC NMR (400MHz, 298K) of **6b** in  $\text{CD}_2\text{Cl}_2$ .

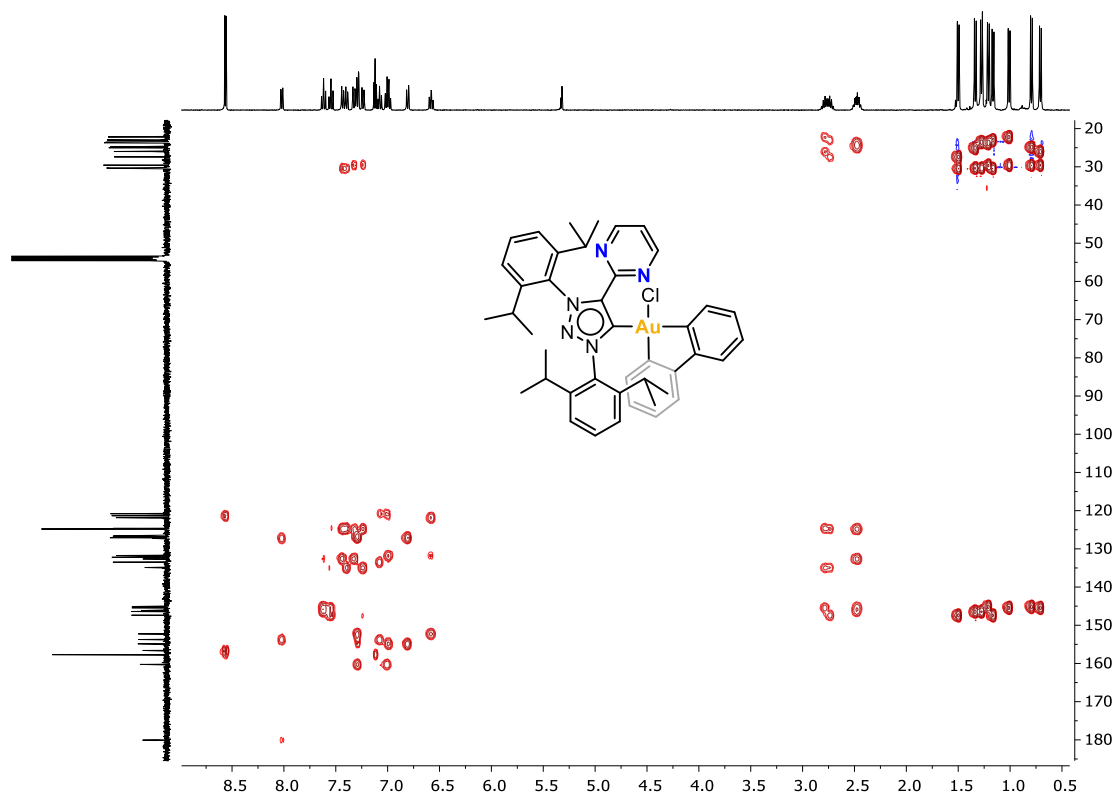


Figure S55.  $^1\text{H}$ ,  $^{13}\text{C}$ -HMBC NMR (400MHz, 298K) of **6b** in  $\text{CD}_2\text{Cl}_2$ .

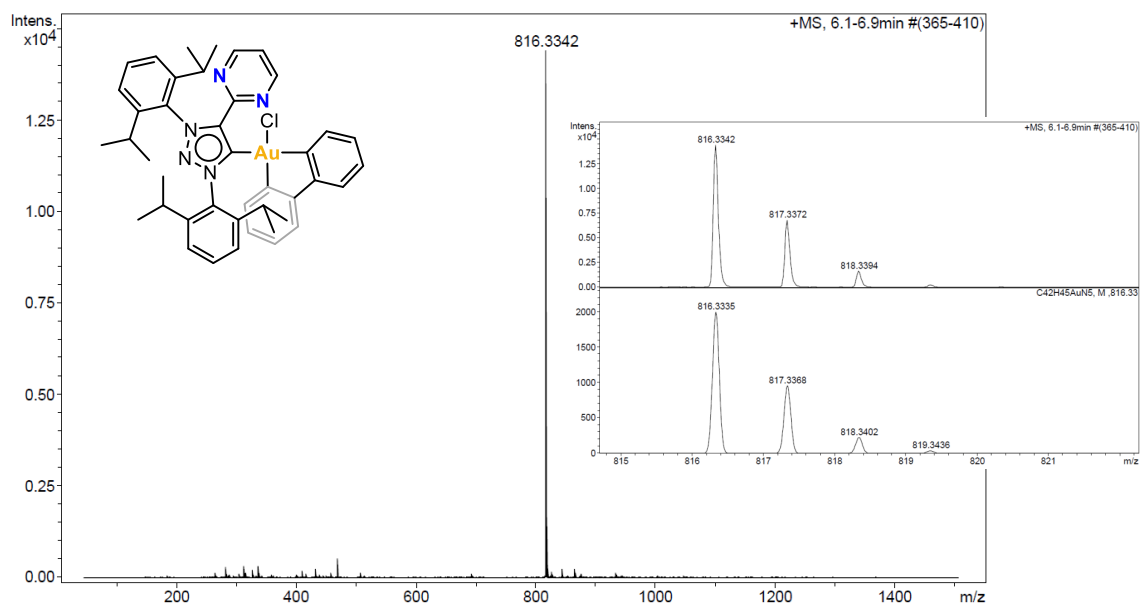
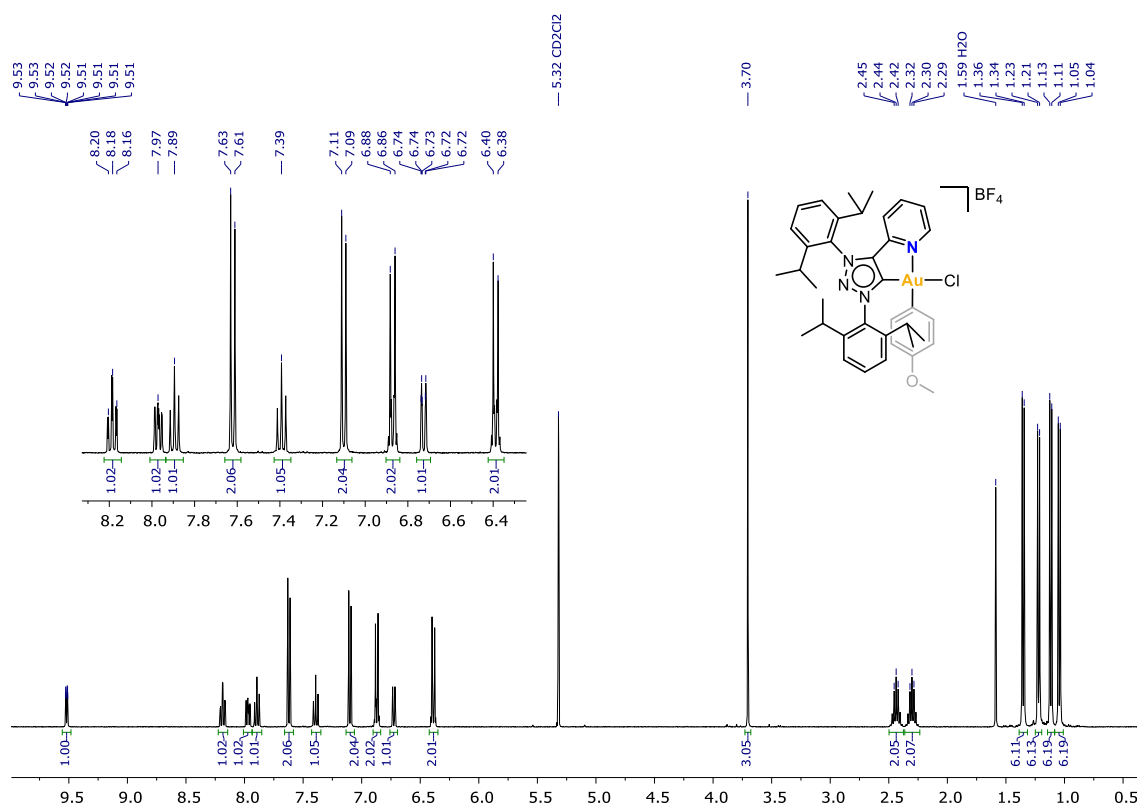
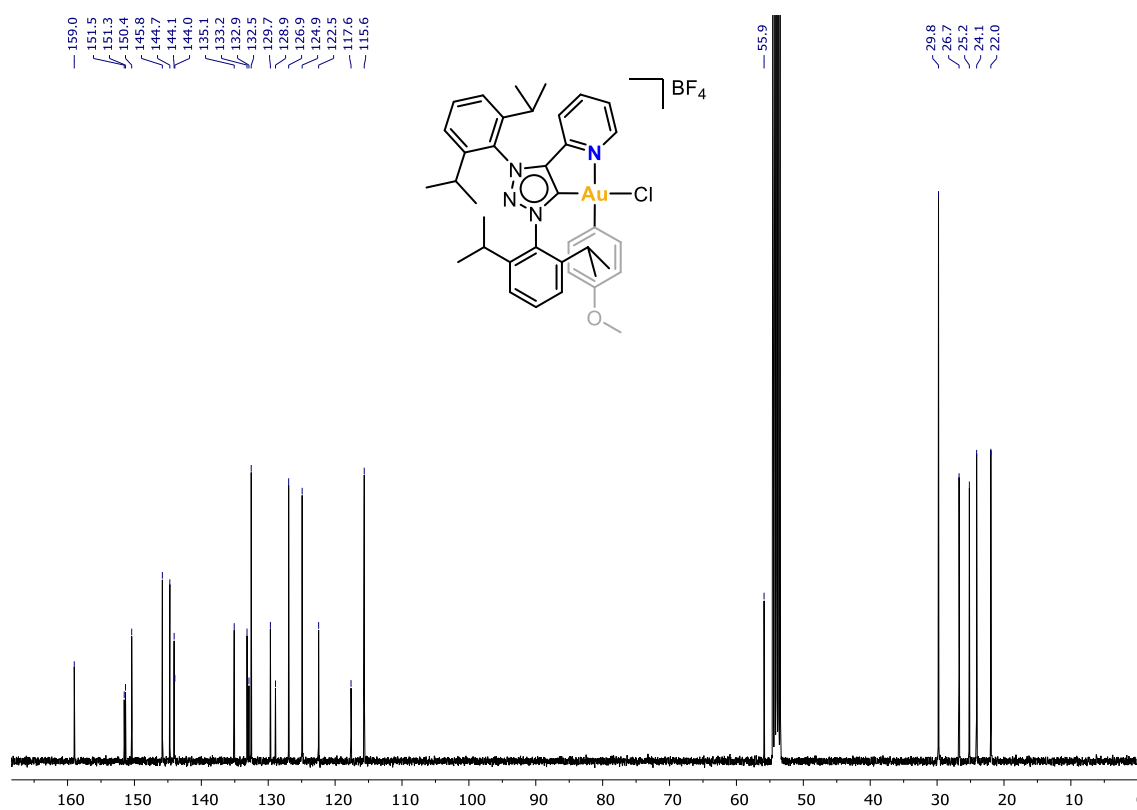


Figure S56. HRMS-ESI(+) of **6b**.

## 8.11 NMR and HRMS-ESI Spectra of complex *cis-7a-Cl*



**Figure S57.**  $^1\text{H}$  NMR (400MHz, 298K) of *cis-7a-Cl* in  $\text{CD}_2\text{Cl}_2$ .



**Figure S58.**  $^{13}\text{C}$  NMR (101MHz, 298K) of *cis-7a-Cl* in  $\text{CD}_2\text{Cl}_2$ .

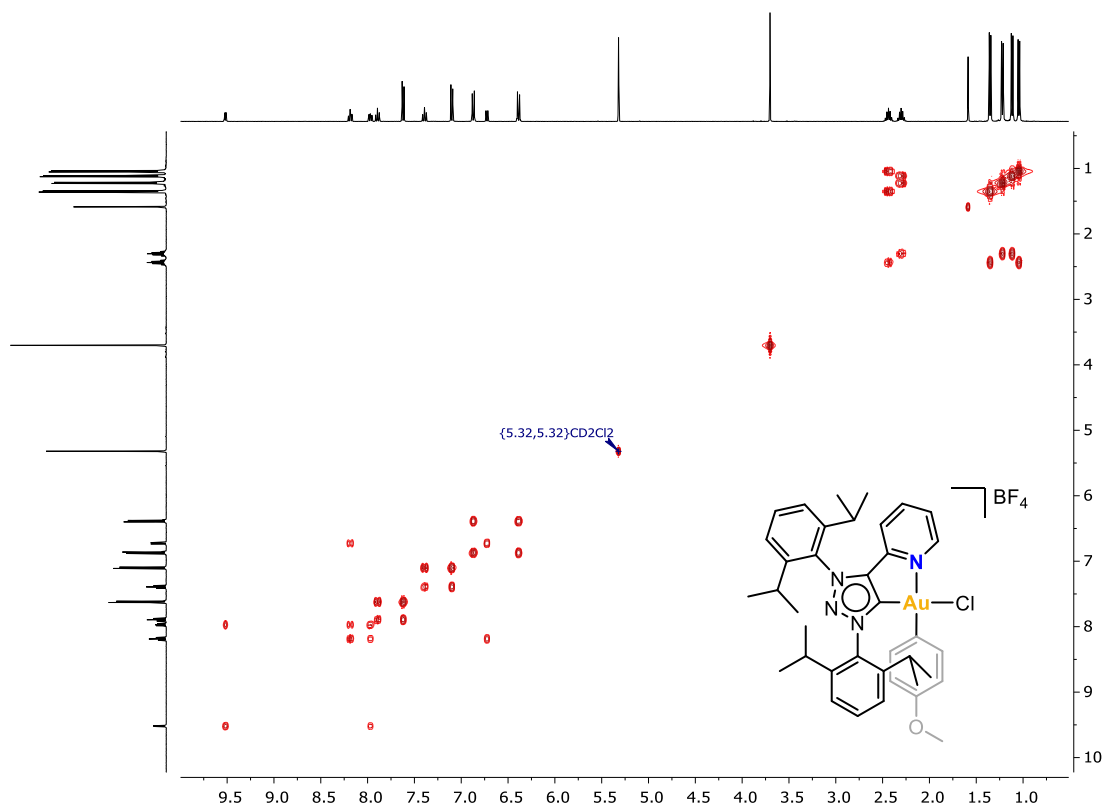


Figure S59.  $^1\text{H}$ ,  $^1\text{H}$ -COSY NMR (400MHz, 298K) of *cis*-7a-Cl in  $\text{CD}_2\text{Cl}_2$ .

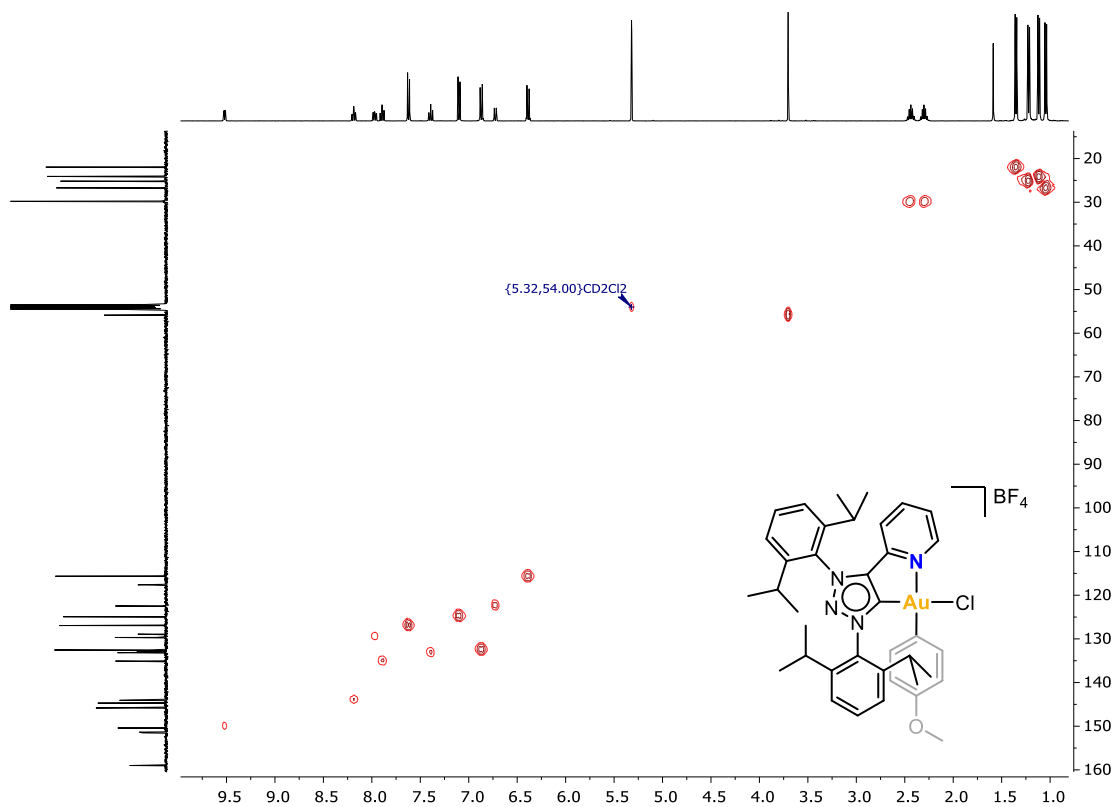


Figure S60.  $^1\text{H}$ ,  $^{13}\text{C}$ -HSQC NMR (400MHz, 298K) of *cis*-7a-Cl in  $\text{CD}_2\text{Cl}_2$ .

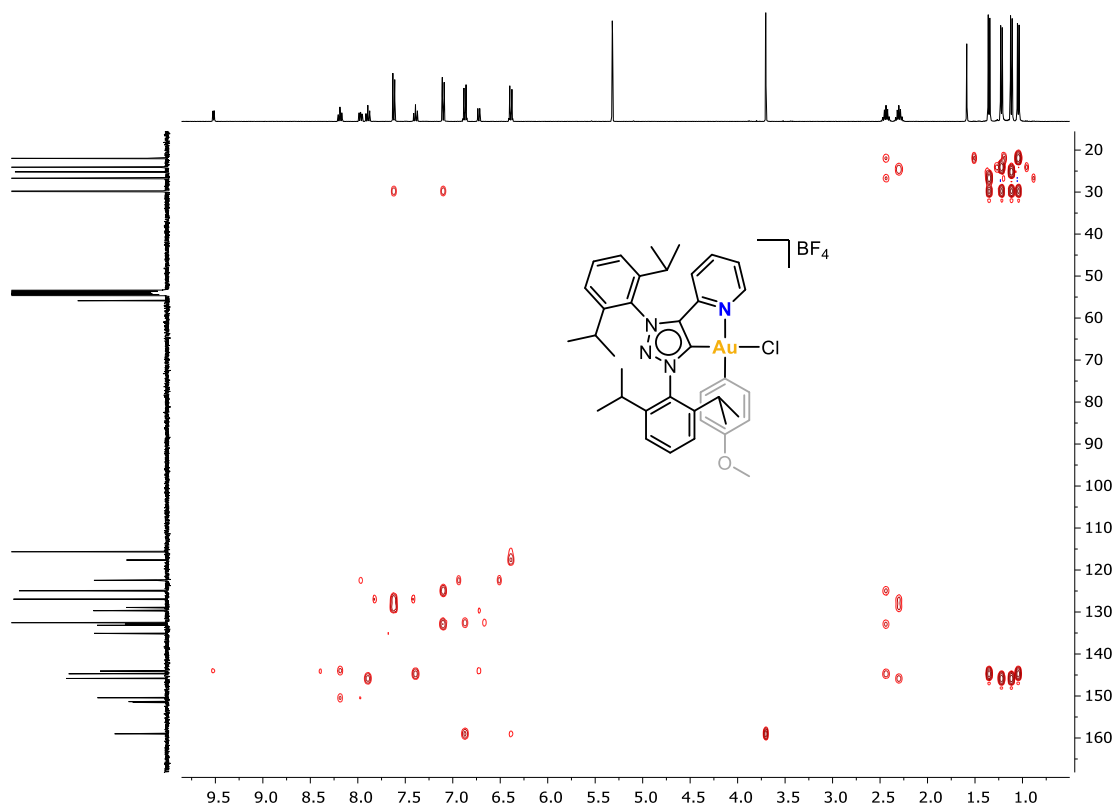


Figure S61.  $^1\text{H}$ ,  $^{13}\text{C}$ -HMBC NMR (400MHz, 298K) of *cis*-7a-Cl in  $\text{CD}_2\text{Cl}_2$ .

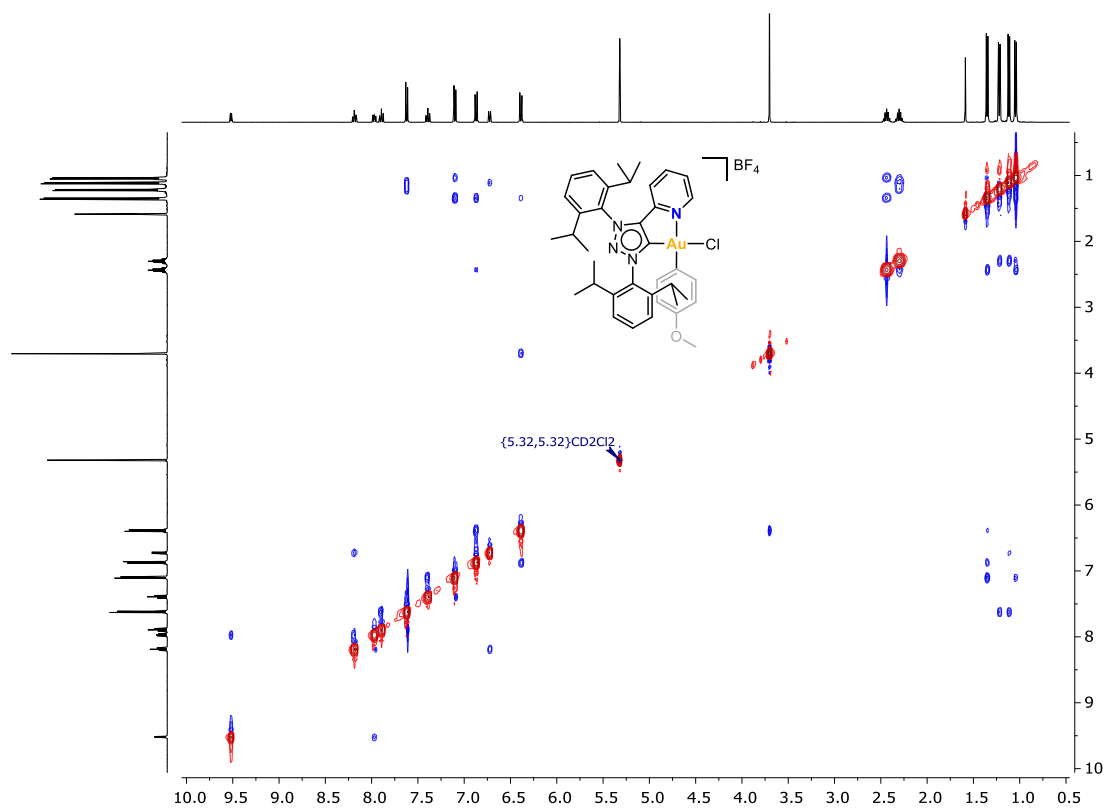


Figure S62.  $^1\text{H}$ ,  $^1\text{H}$ -NOESY NMR (400MHz, 248K) of *cis*-7a-Cl in  $\text{CD}_2\text{Cl}_2$ .

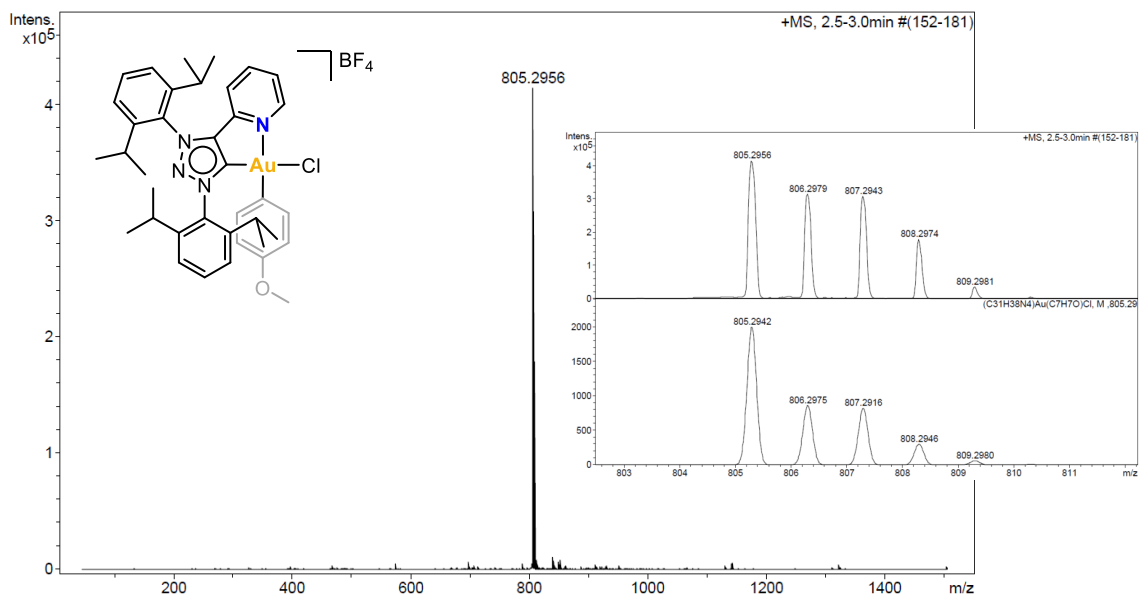


Figure S63. HRMS-ESI(+) of *cis*-7a-Cl.

## 8.12 NMR and HRMS-ESI Spectra of compound 8b-OMe

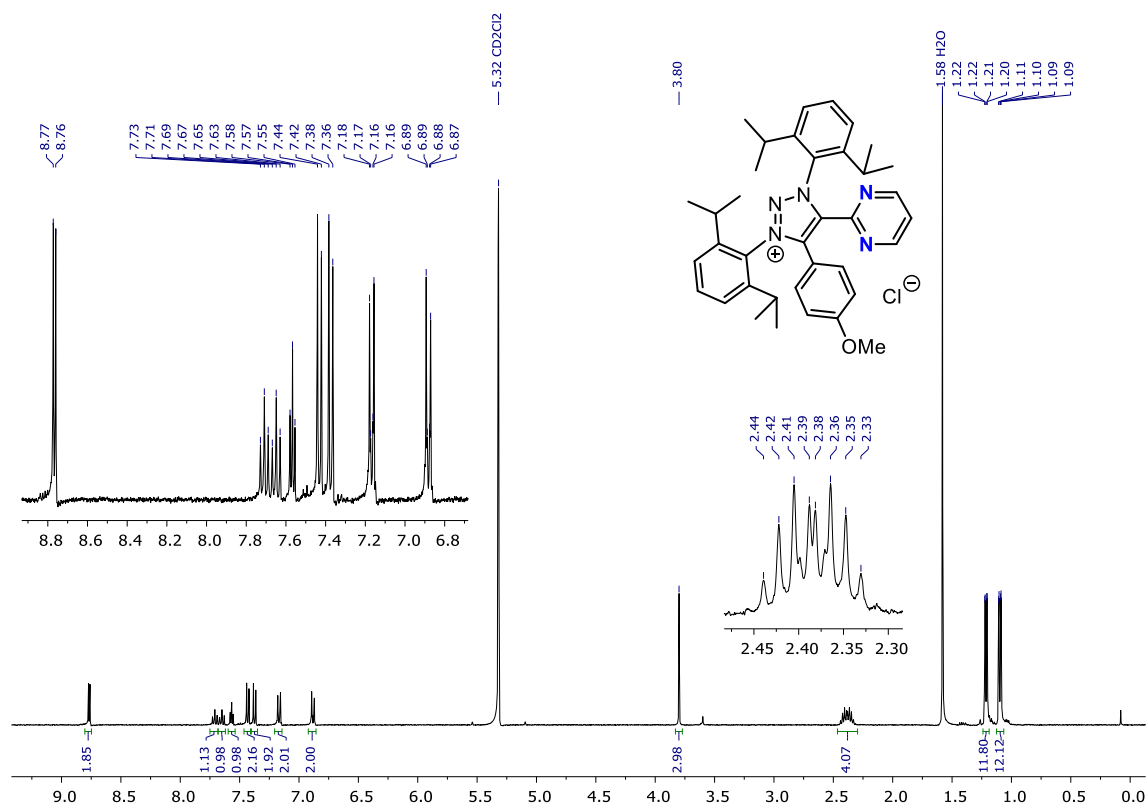


Figure S64. <sup>1</sup>H NMR (400MHz, 298K) of 8b-OMe in CD<sub>2</sub>Cl<sub>2</sub>.

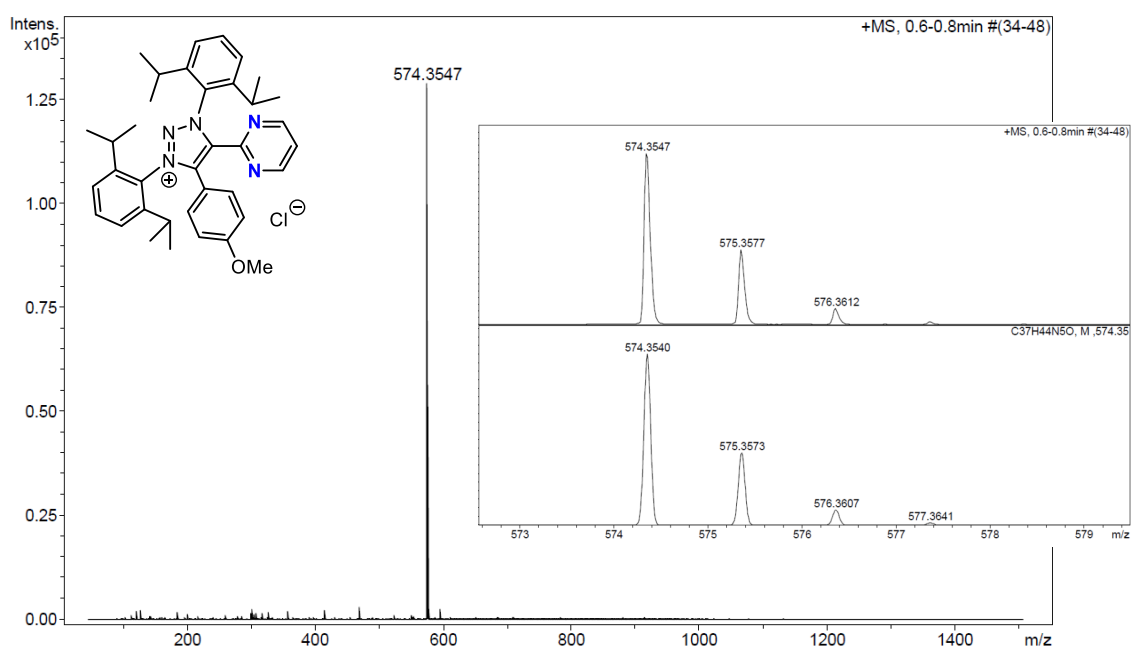


Figure S65. HRMS-ESI(+) of 8b-OMe.



### 8.13 NMR and HRMS-ESI Spectra of compound 8a-Me

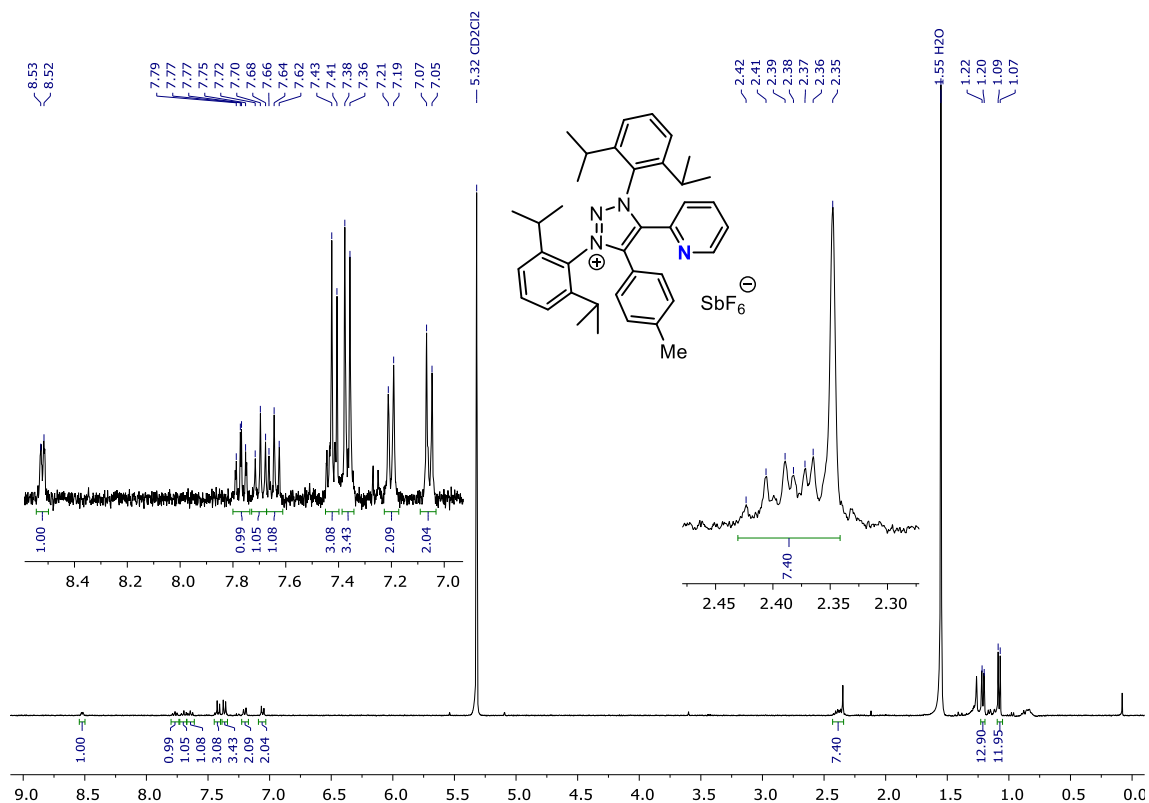


Figure S66.  $^1\text{H}$  NMR (400MHz, 298K) of 8a-Me in  $\text{CD}_2\text{Cl}_2$ .

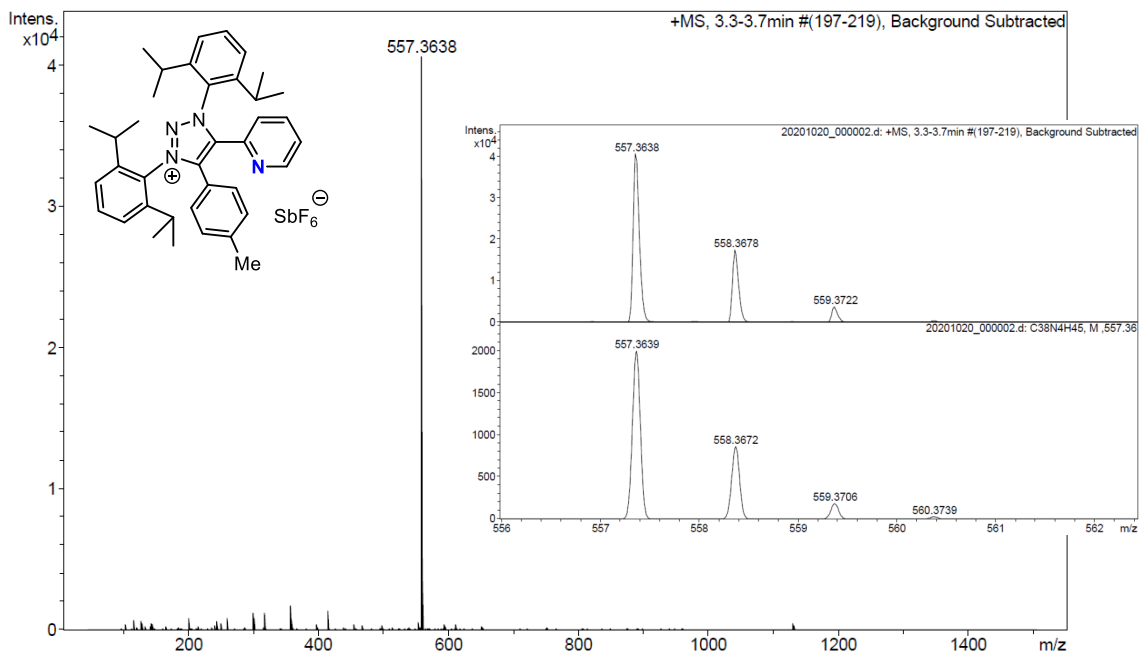
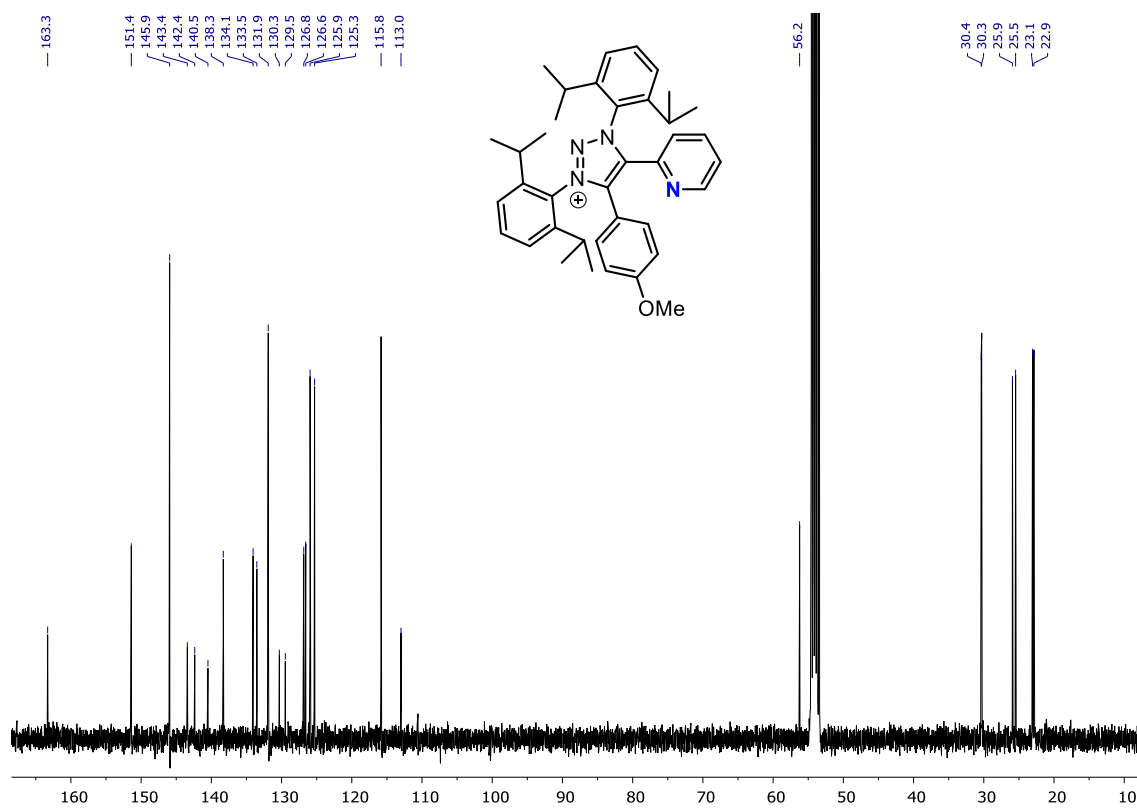
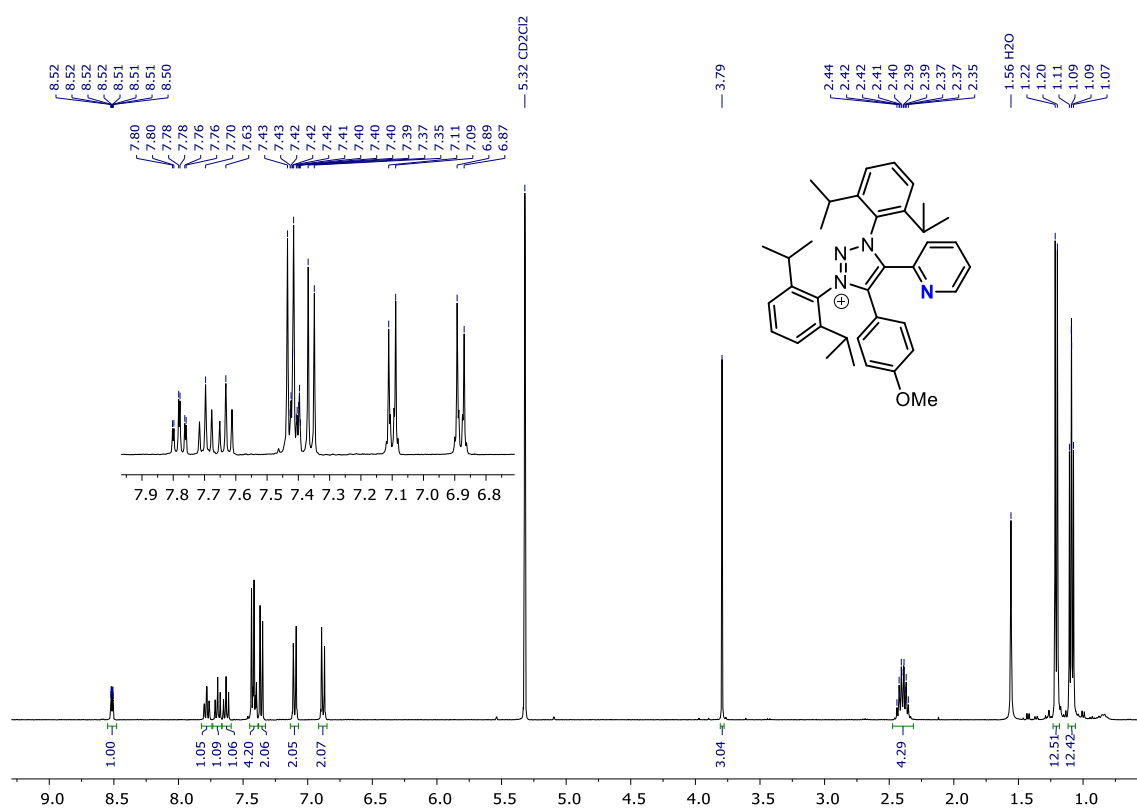


Figure S67. HRMS-ESI(+) of 8a-Me.

## 8.14 NMR and HRMS-ESI Spectra of compound 8a-OMe



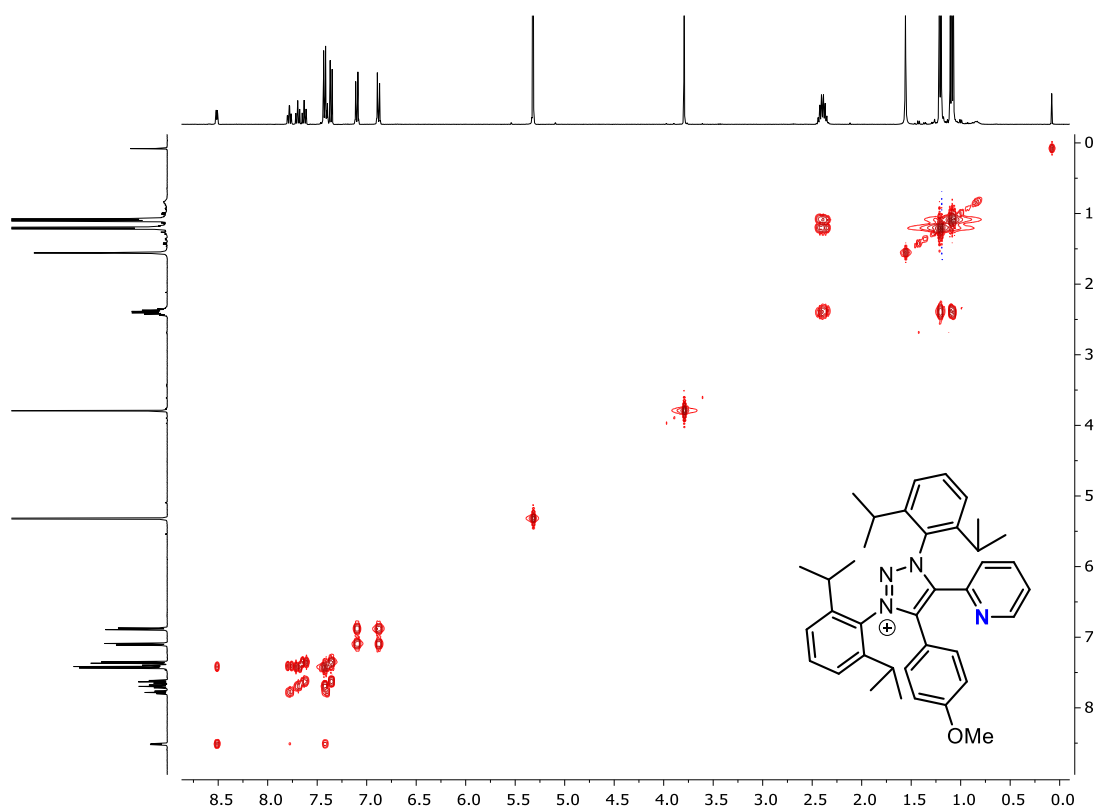


Figure S70.  $^1\text{H}$ ,  $^1\text{H}$ -COSY NMR (400MHz, 298K) of **8a-OMe** in  $\text{CD}_2\text{Cl}_2$ .

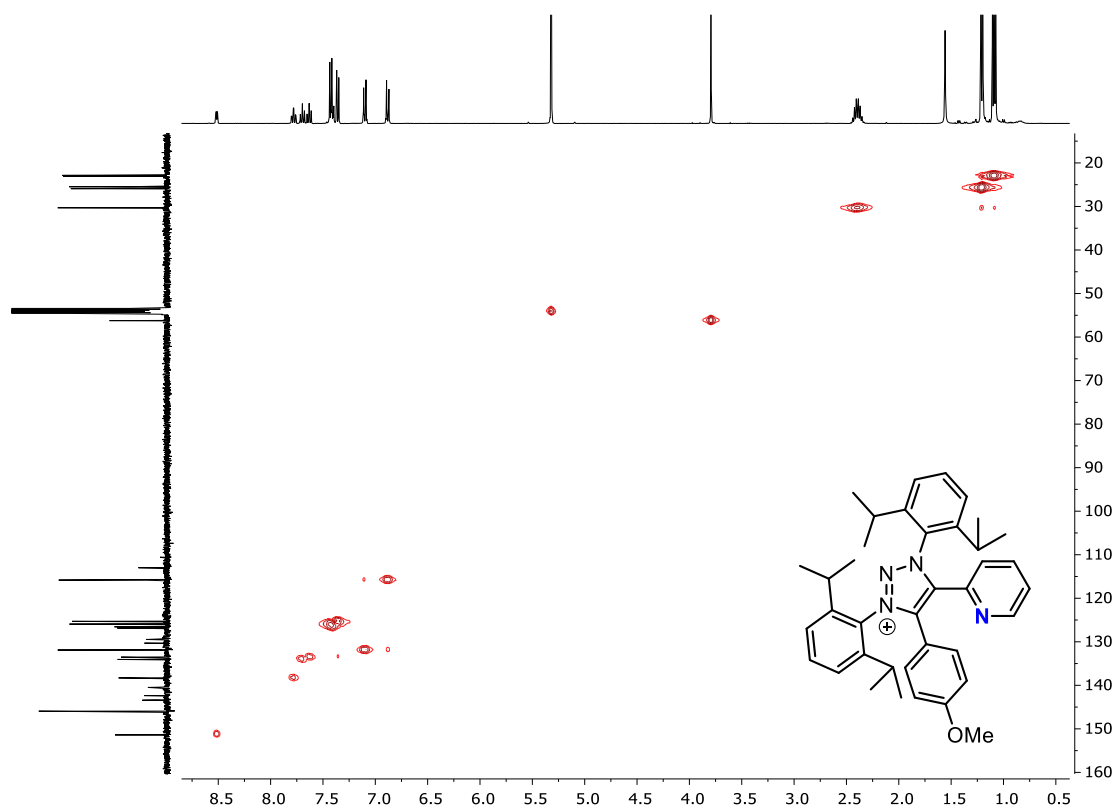
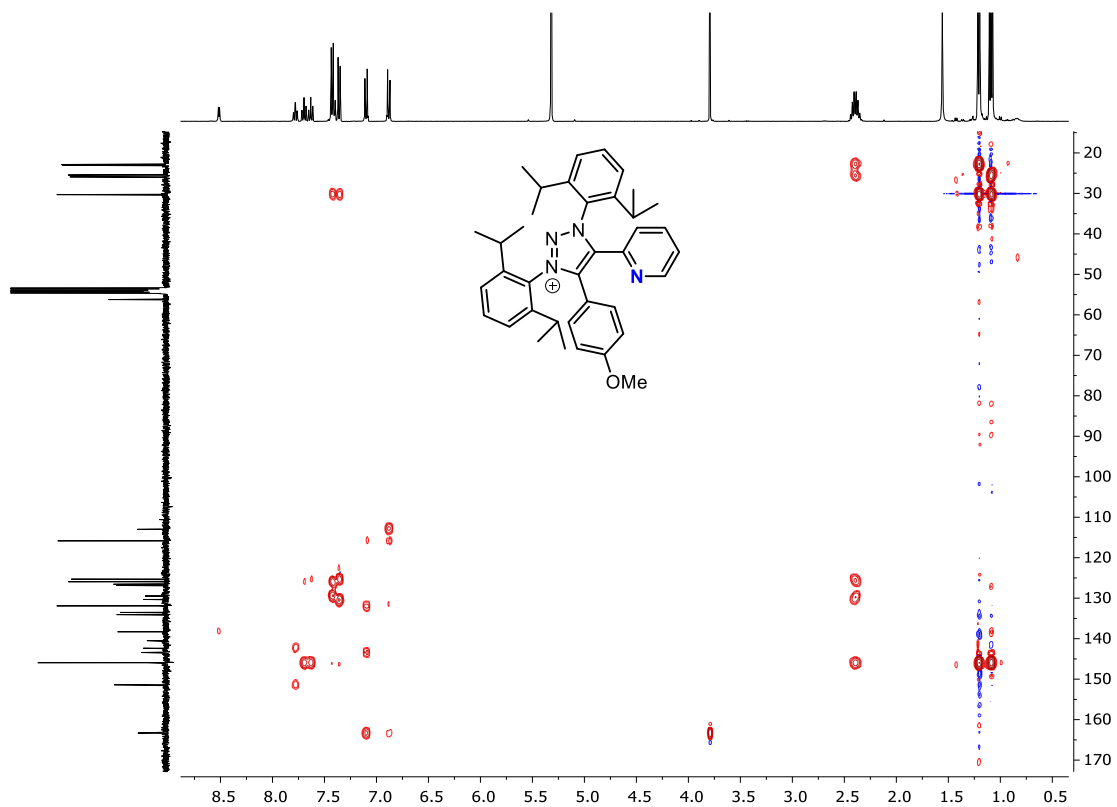
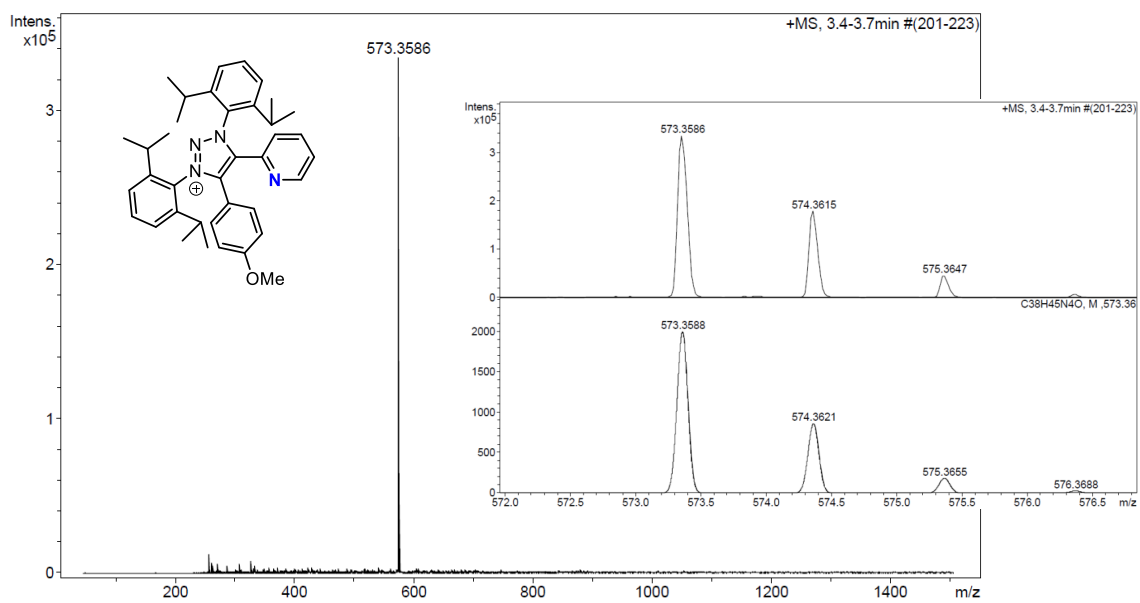


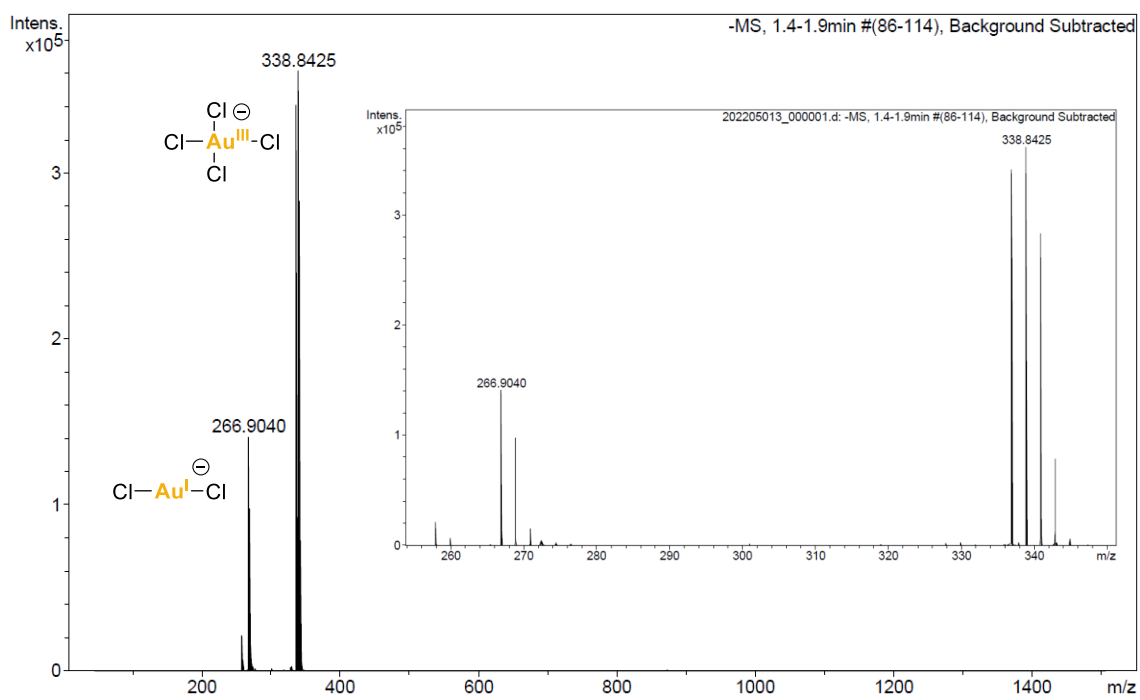
Figure S71.  $^1\text{H}$ ,  $^{13}\text{C}$ -HSQC NMR (400MHz, 298K) of **8a-OMe** in  $\text{CD}_2\text{Cl}_2$ .



**Figure S72.**  $^1\text{H}$ ,  $^{13}\text{C}$ -HMBC NMR (400MHz, 298K) of **8a-OMe** in  $\text{CD}_2\text{Cl}_2$ .



**Figure S73.** HRMS-ESI(+) of **8a-OMe**.



**Figure S74.** HRMS-ESI(-) of **8a-OMe**.

## 8.15 NMR Spectra of compound 10

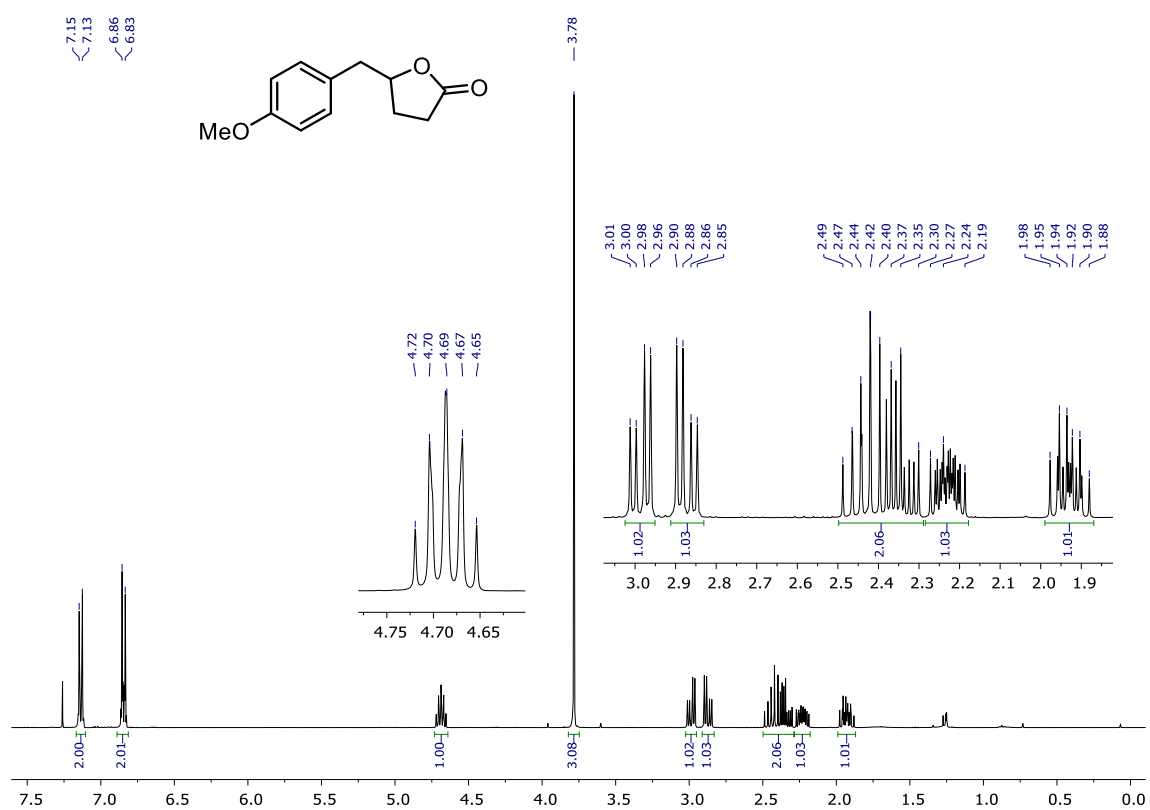


Figure S75. <sup>1</sup>H NMR (400MHz, 298K) of 10 in CDCl<sub>3</sub>.

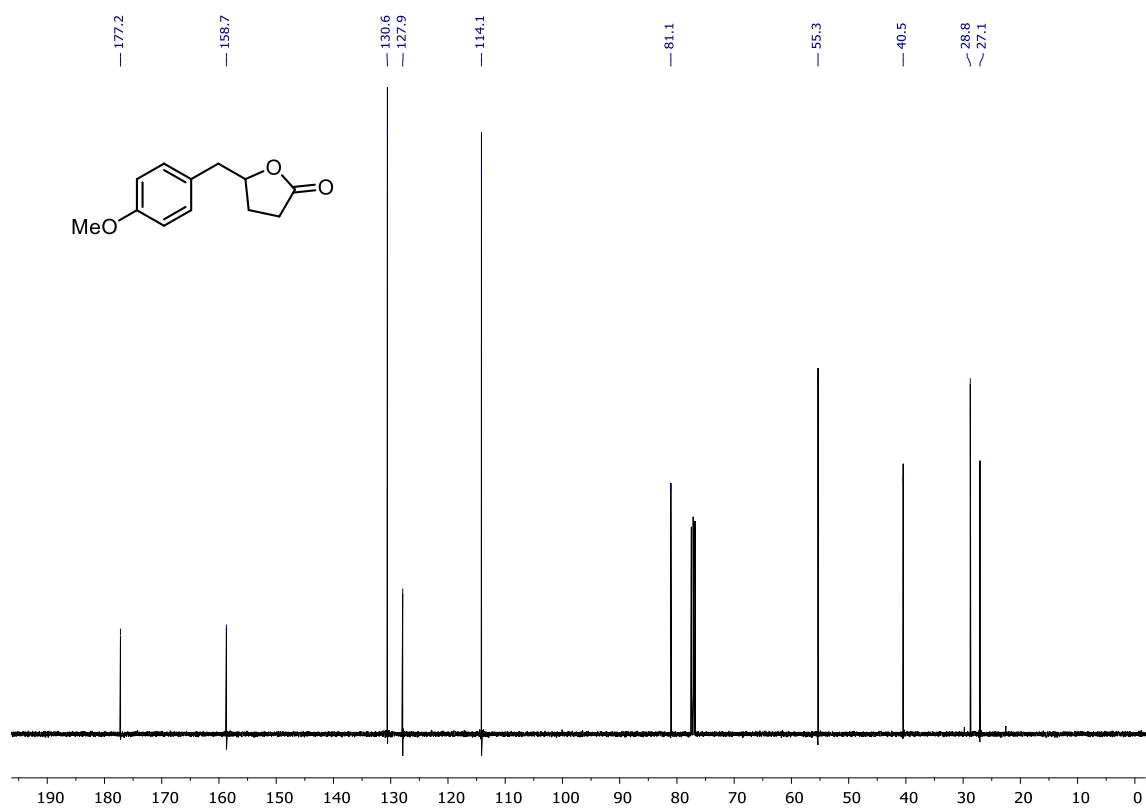


Figure S76. <sup>13</sup>C NMR (101MHz, 298K) of 10 in CDCl<sub>3</sub>.

## 8.16 NMR and HRMS-ESI Spectra of compound 15

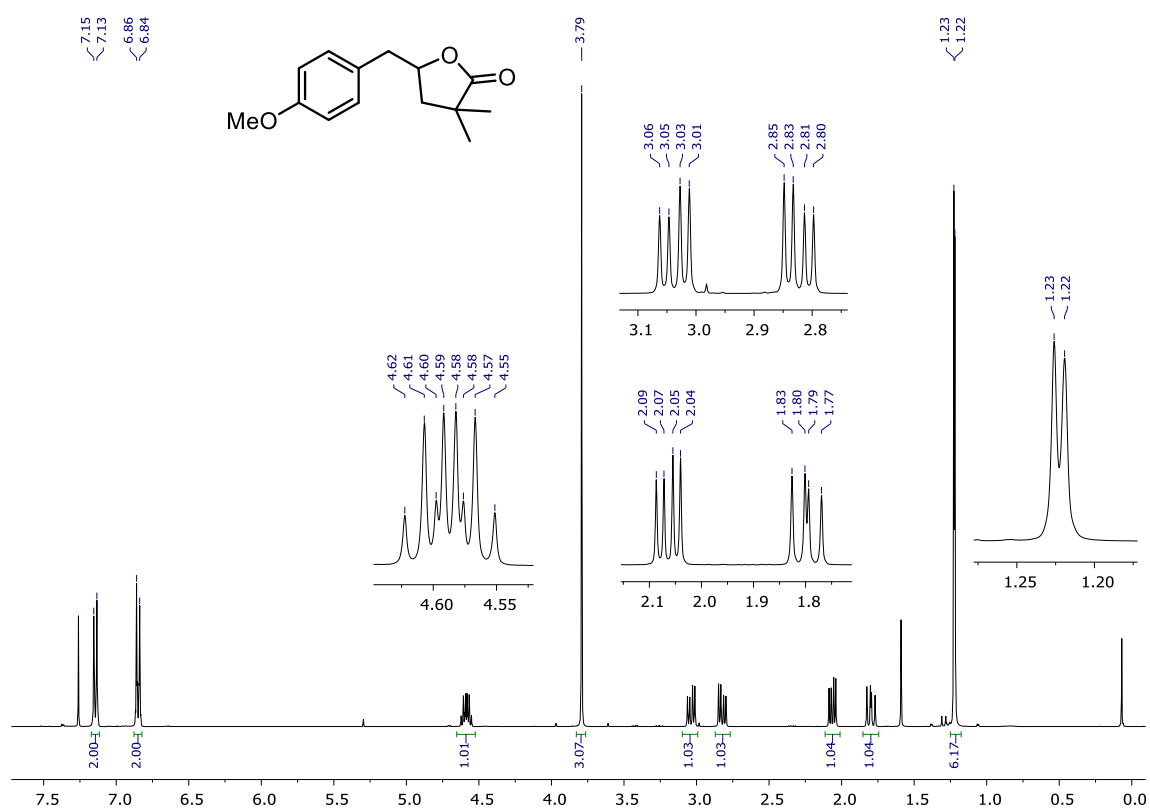


Figure S77.  $^1\text{H NMR}$  (400MHz, 298K) of 15 in  $\text{CDCl}_3$ .

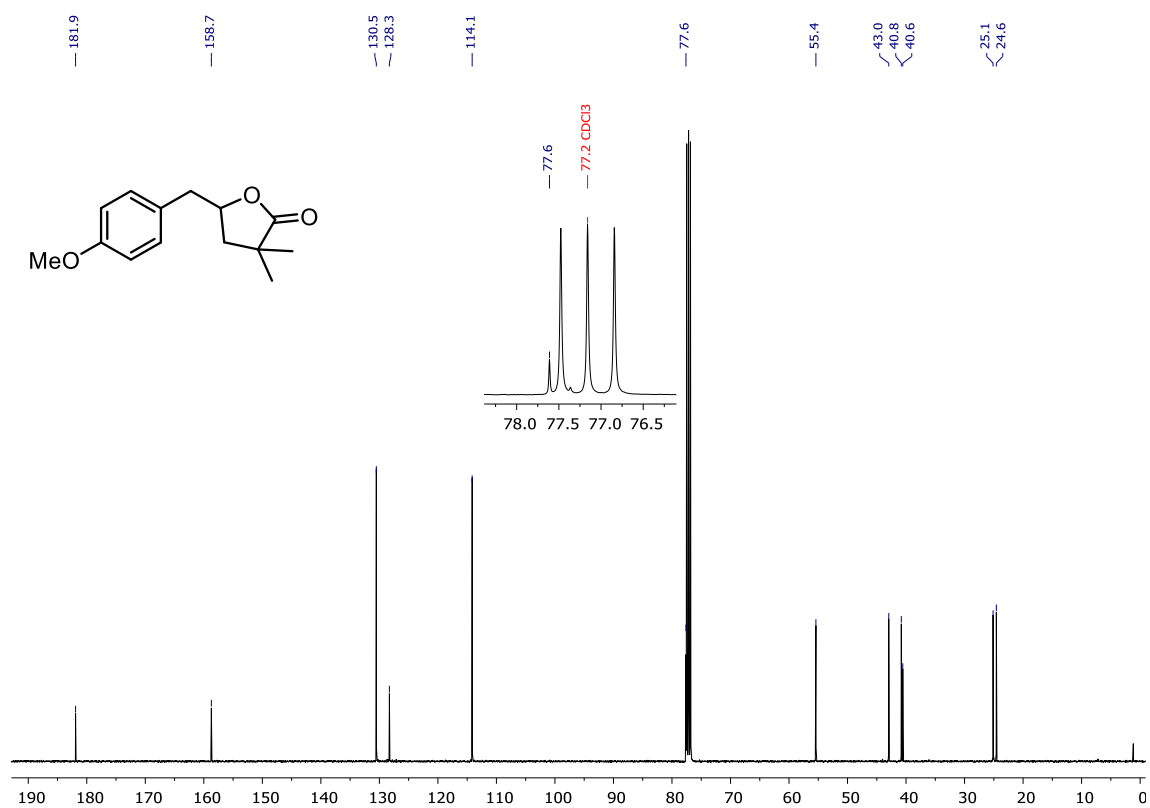
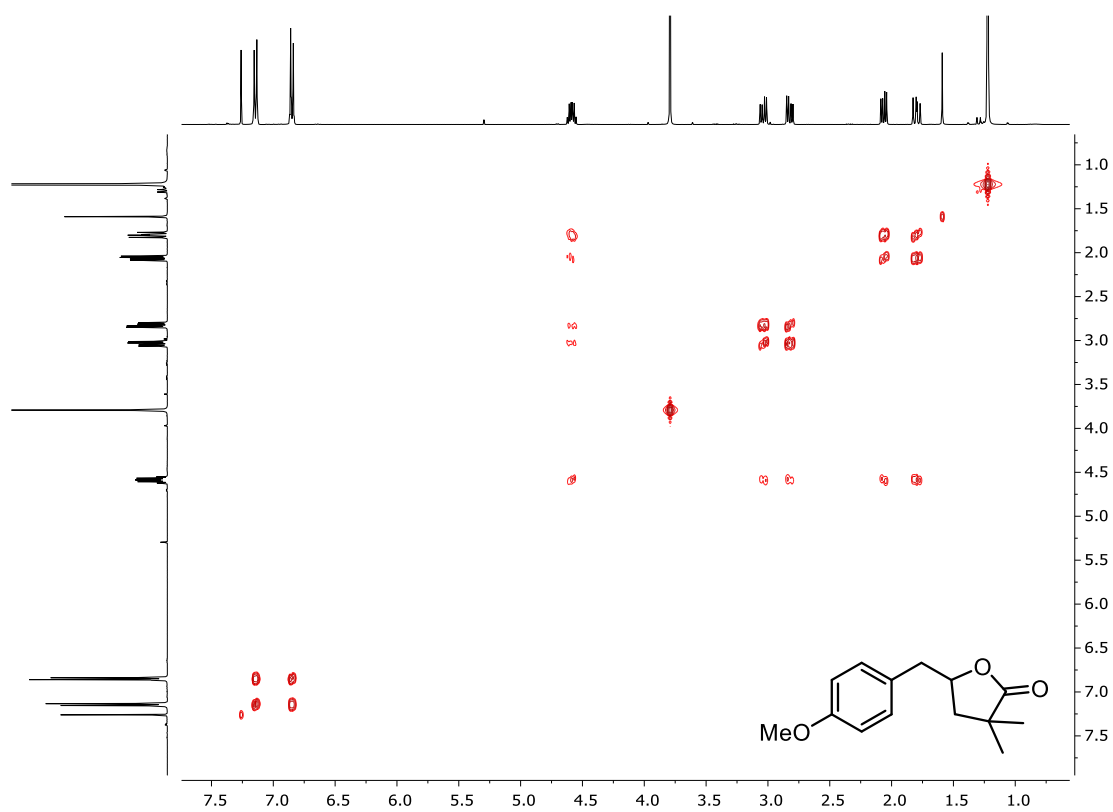
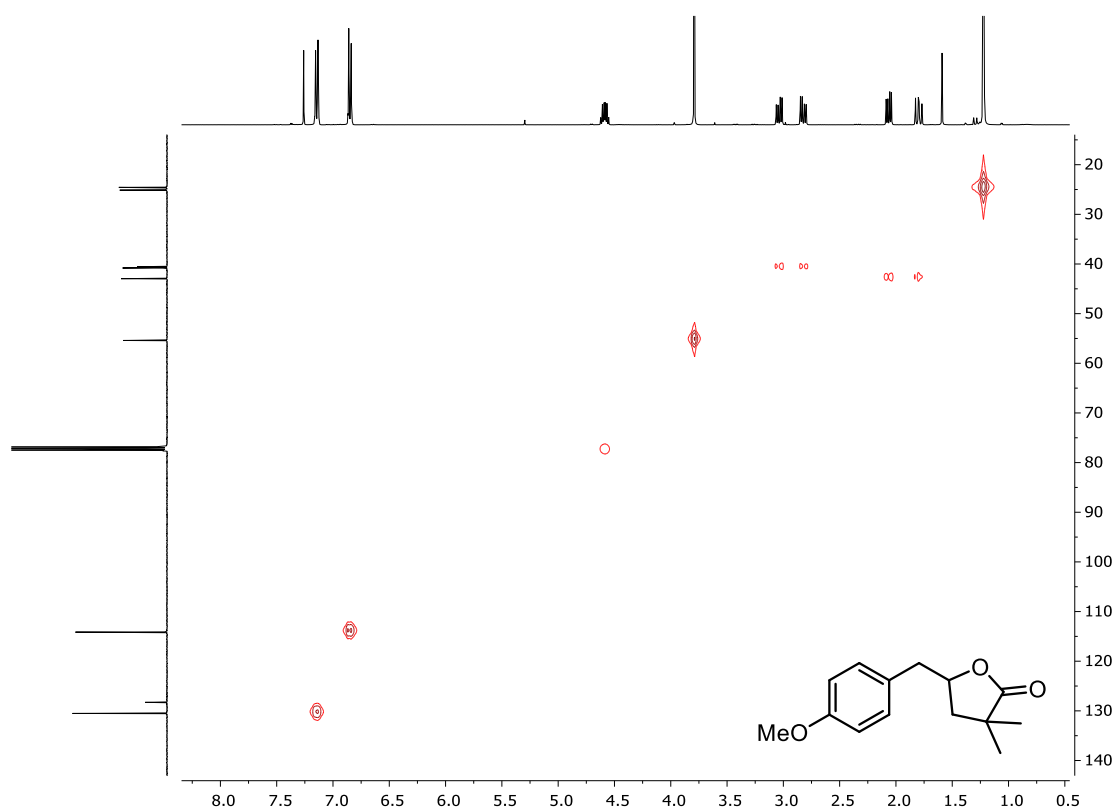


Figure S78.  $^{13}\text{C NMR}$  (101MHz, 298K) of 15 in  $\text{CDCl}_3$ .

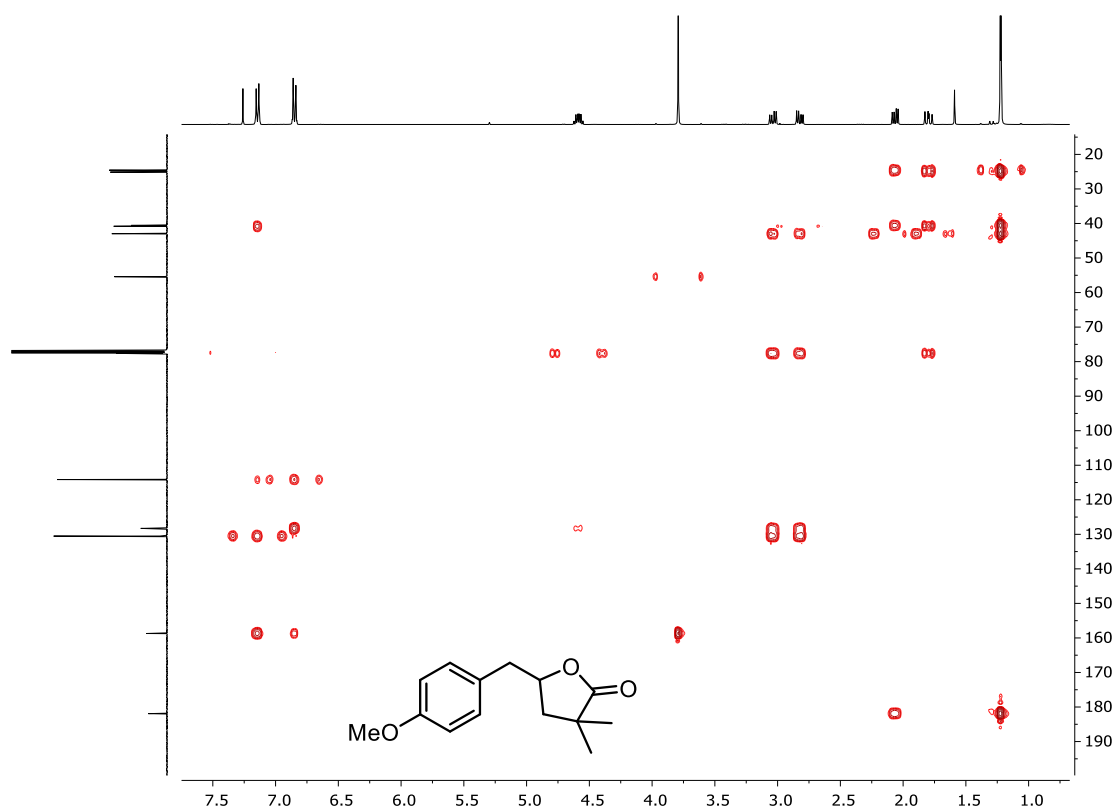


**Figure S79.**  $^1\text{H}$ ,  $^1\text{H}$ -COSY NMR (400MHz, 298K) of **15** in  $\text{CDCl}_3$ .

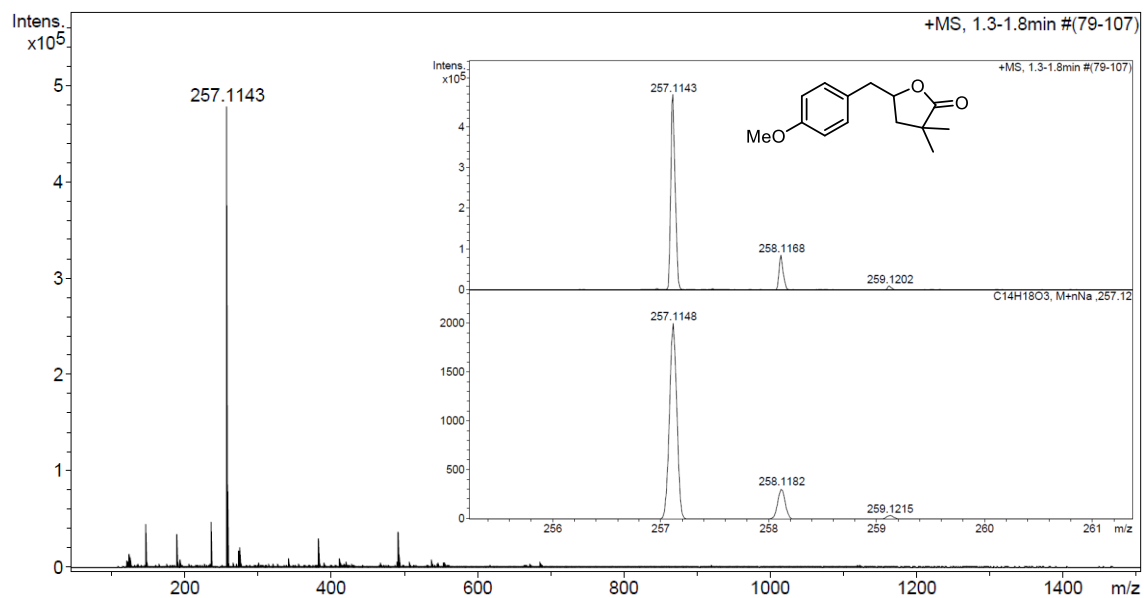


**Figure S80.**  $^1\text{H}$ ,  $^{13}\text{C}$ -HSQC NMR (400MHz, 298K) of **15** in  $\text{CDCl}_3$ .



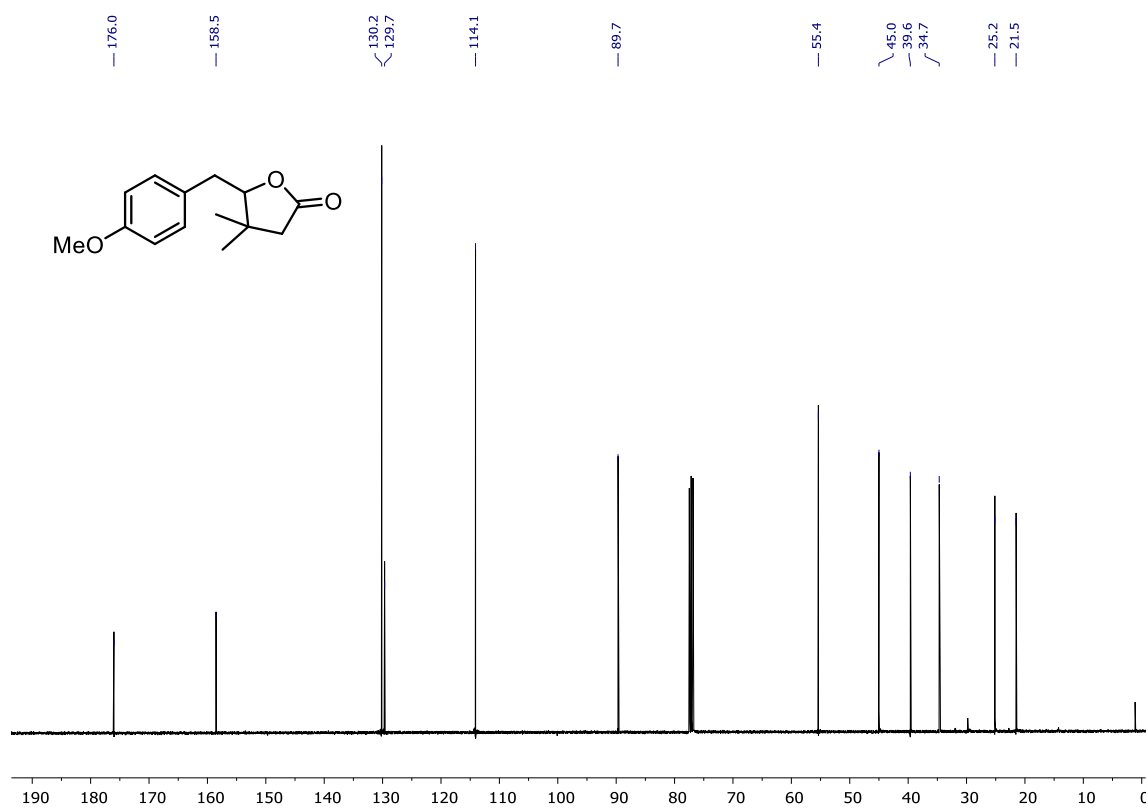
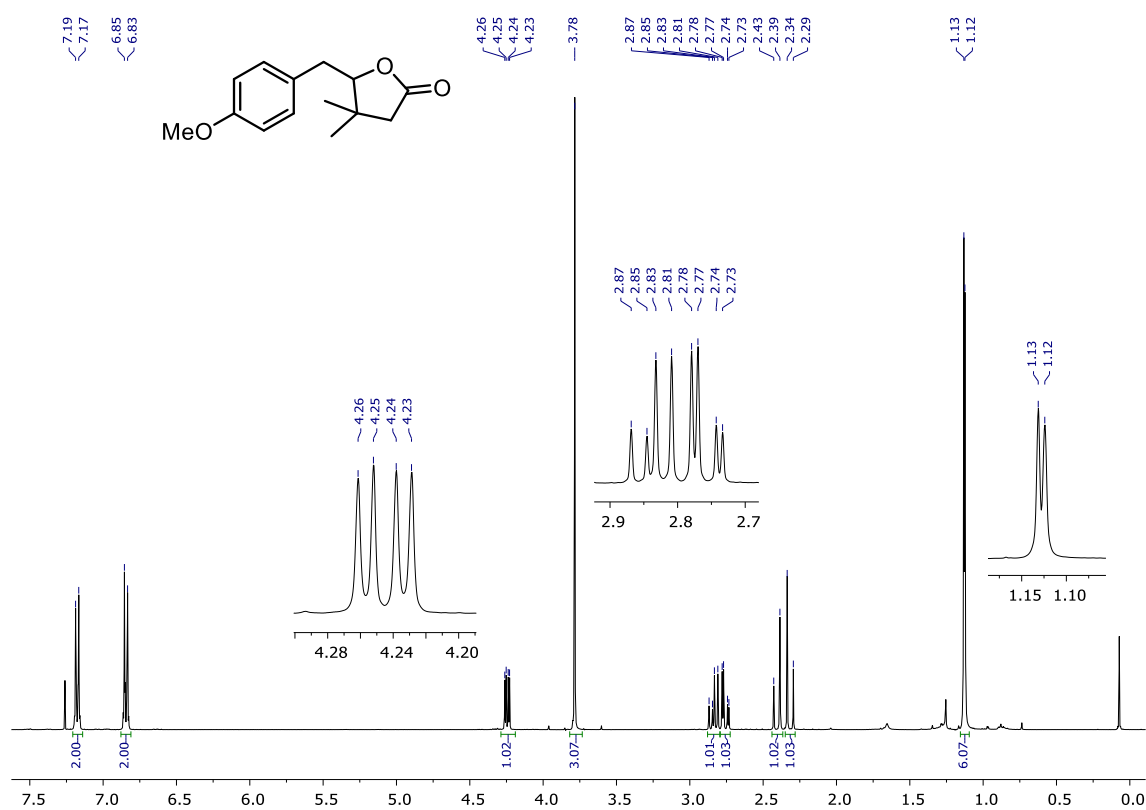


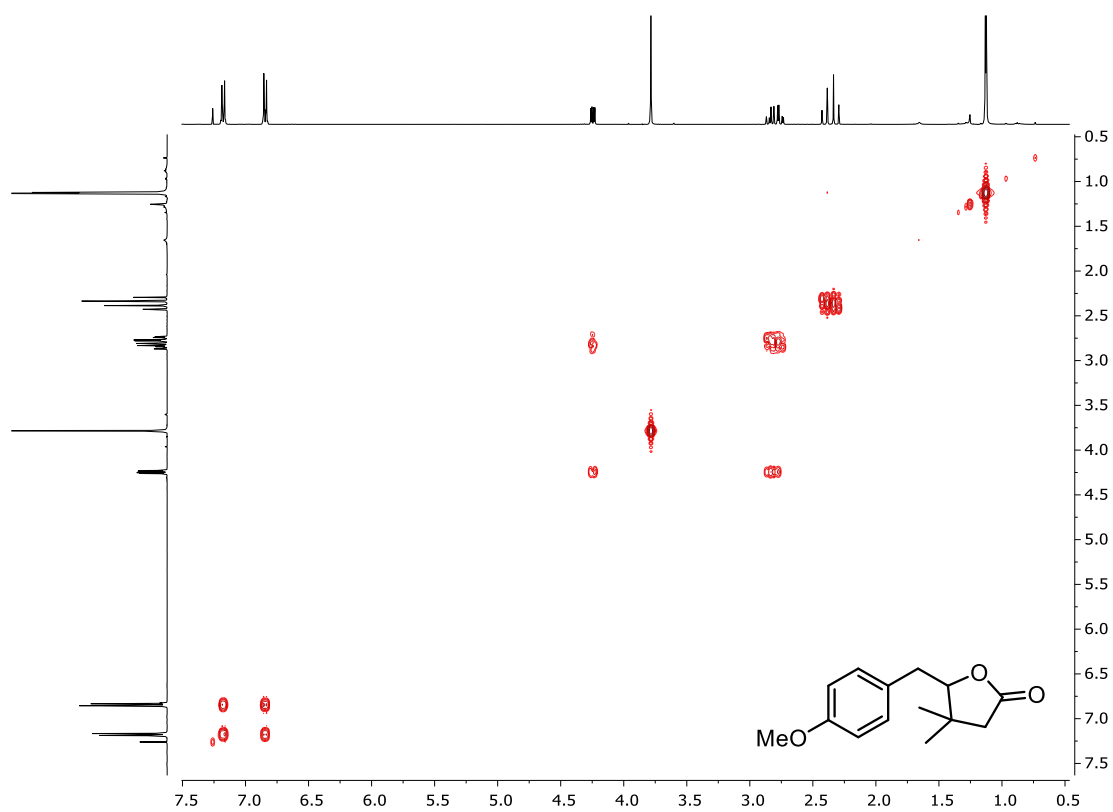
**Figure S81.**  $^1\text{H}$ ,  $^{13}\text{C}$ -HMBC NMR (400MHz, 298K) of **15** in  $\text{CDCl}_3$ .



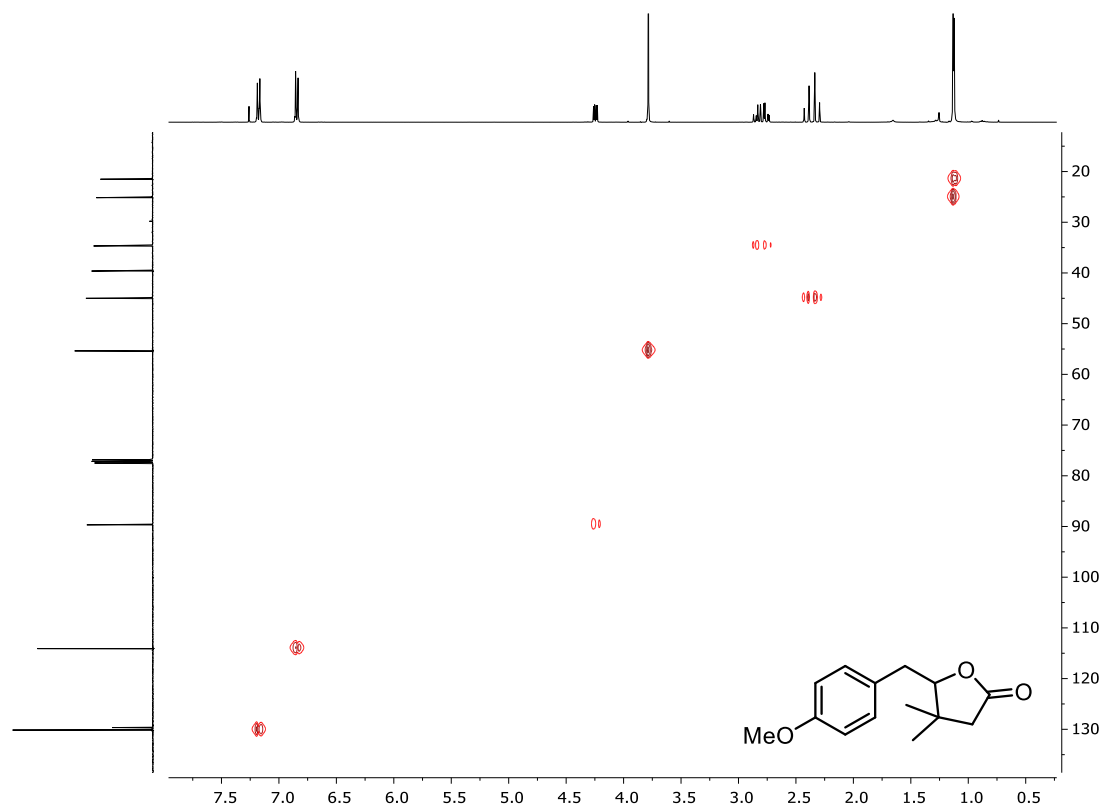
**Figure S82.** HRMS-ESI(+) of **15**.

## 8.17 NMR and HRMS-ESI Spectra of compound 16

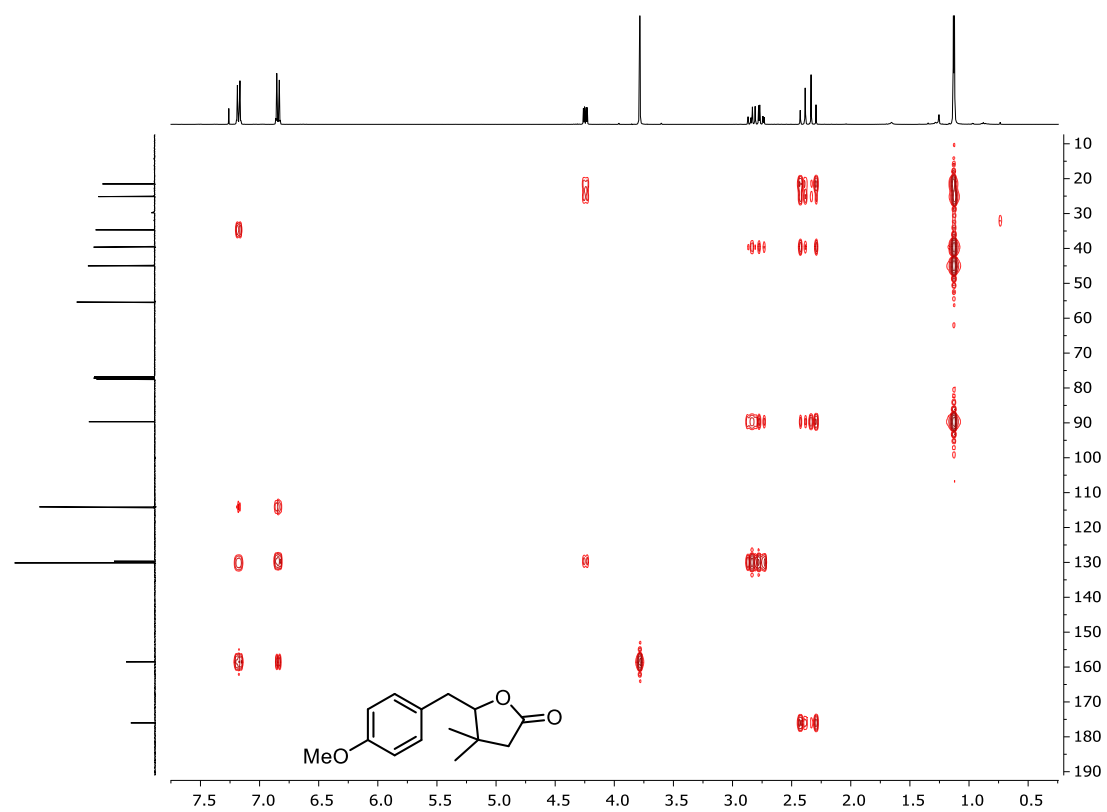




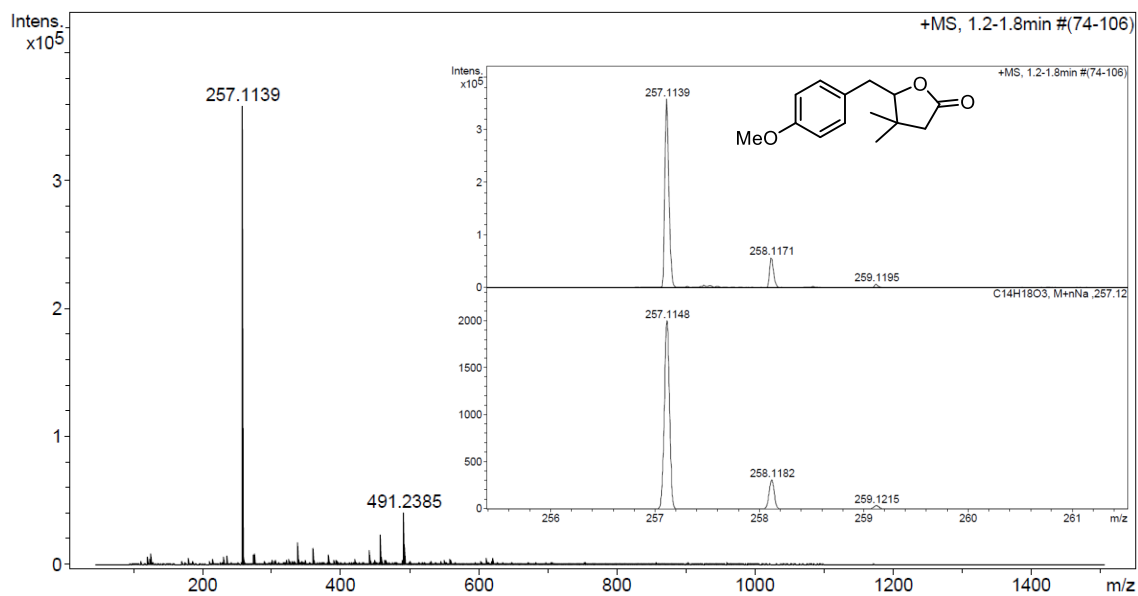
**Figure S85.**  $^1\text{H}$ ,  $^1\text{H}$ -COSY NMR (400MHz, 298K) of **16** in  $\text{CDCl}_3$ .



**Figure S86.**  $^1\text{H}$ ,  $^{13}\text{C}$ -HSQC NMR (400MHz, 298K) of **16** in  $\text{CDCl}_3$ .



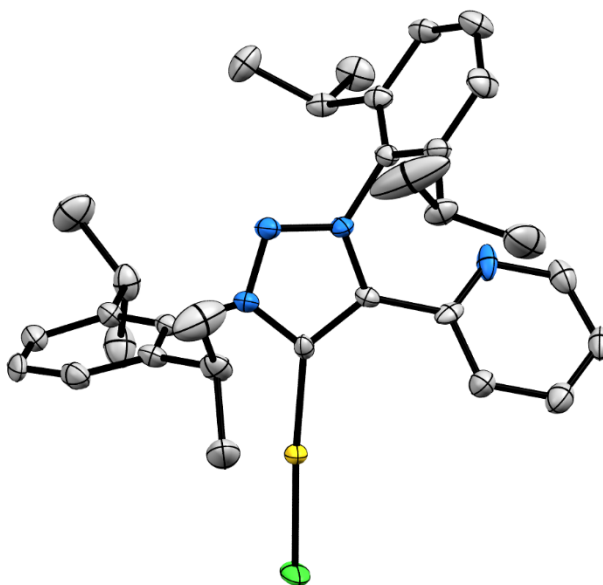
**Figure S87.**  $^1\text{H}$ ,  $^{13}\text{C}$ -HMBC NMR (400MHz, 298K) of **16** in  $\text{CDCl}_3$ .



**Figure S88.** HRMS-ESI(+) of **16**.

## 9. X-Ray structures and crystallographic data

### 9.1 Complex 2a



**Figure S89.** Crystal structure of **2a** (CCDC 2163609). Ellipsoids set at 50% probability; H atoms removed for clarity.

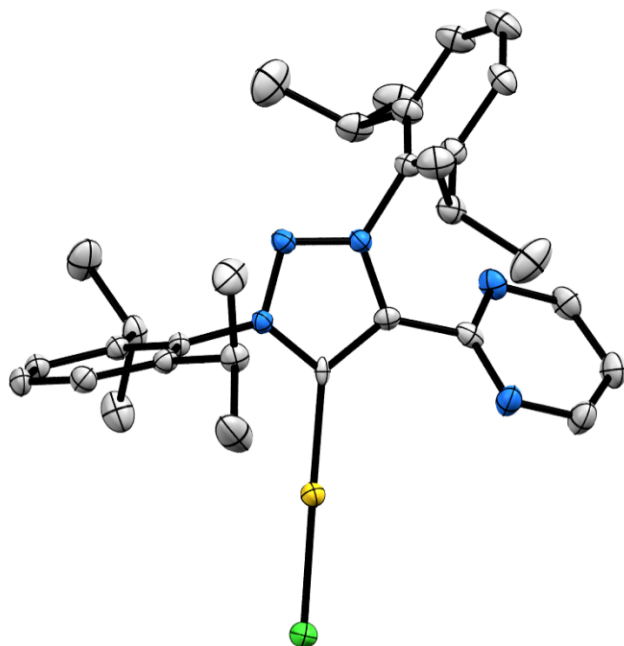
**Table S7.** Crystallographic parameters for **2a**.

<b>Chemical formula</b>	C <sub>31</sub> H <sub>38</sub> AuClN <sub>4</sub>	
<b>Formula weight</b>	699.07 g/mol	
<b>Temperature</b>	100(2) K	
<b>Wavelength</b>	0.71073 Å	
<b>Crystal size</b>	0.050 x 0.100 x 0.150 mm	
<b>Crystal system</b>	Monoclinic	
<b>Space group</b>	P 1 21/n 1	
<b>Unit cell dimensions</b>	a = 9.9684(5) Å	α = 90°
	b = 23.6287(10) Å	β = 101.309(2)°
	c = 12.9108(6) Å	γ = 90°
<b>Volume</b>	2982.0(2) Å <sup>3</sup>	
<b>Density (calculated)</b>	1.557 g/cm <sup>3</sup>	
<b>Absorption coefficient</b>	5.049 mm <sup>-1</sup>	
<b>Final R indices</b>	5846 data; I > 2σ(I)	R1 = 0.0473, wR2 = 0.1253
	All data	R1 = 0.0594, wR2 = 0.1360

A colorless prism-like specimen of C<sub>31</sub>H<sub>38</sub>AuClN<sub>4</sub>, approximate dimensions 0.050 mm x 0.100 mm x 0.150 mm, was used for the X-ray crystallographic analysis. The X-ray

intensity data were measured on a D8 QUEST ECO three-circle diffractometer system equipped with a Ceramic x-ray tube (Mo K $\alpha$ ,  $\lambda = 0.71073 \text{ \AA}$ ) and a doubly curved silicon crystal Bruker Triumph monochromator. A total of 907 frames were collected. The total exposure time was 2.52 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 116918 reflections to a maximum  $\theta$  angle of  $27.62^\circ$  ( $0.77 \text{ \AA}$  resolution), of which 6893 were independent (average redundancy 16.962, completeness = 99.5%,  $R_{\text{int}} = 6.18\%$ ,  $R_{\text{sig}} = 2.32\%$ ) and 5846 (84.81%) were greater than  $2\sigma(F^2)$ . The final cell constants of  $a = 9.9684(5) \text{ \AA}$ ,  $b = 23.6287(10) \text{ \AA}$ ,  $c = 12.9108(6) \text{ \AA}$ ,  $\beta = 101.309(2)^\circ$ , volume =  $2982.0(2) \text{ \AA}^3$ , are based upon the refinement of the XYZ-centroids of 9612 reflections above  $20 \sigma(I)$  with  $5.743^\circ < 2\theta < 54.88^\circ$ . Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.779. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.5180 and 0.7860. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group  $P 1 21/n 1$ , with  $Z = 4$  for the formula unit,  $C_{31}H_{38}AuClN_4$ . The final anisotropic full-matrix least-squares refinement on  $F^2$  with 342 variables converged at  $R1 = 4.73\%$ , for the observed data and  $wR2 = 13.60\%$  for all data. The goodness-of-fit was 1.088. The largest peak in the final difference electron density synthesis was  $7.653 \text{ e}^-/\text{\AA}^3$  and the largest hole was  $-1.434 \text{ e}^-/\text{\AA}^3$  with an RMS deviation of  $0.206 \text{ e}^-/\text{\AA}^3$ . On the basis of the final model, the calculated density was  $1.557 \text{ g/cm}^3$  and  $F(000)$ , 1392  $e^-$ .

## 9.2 Complex 2b



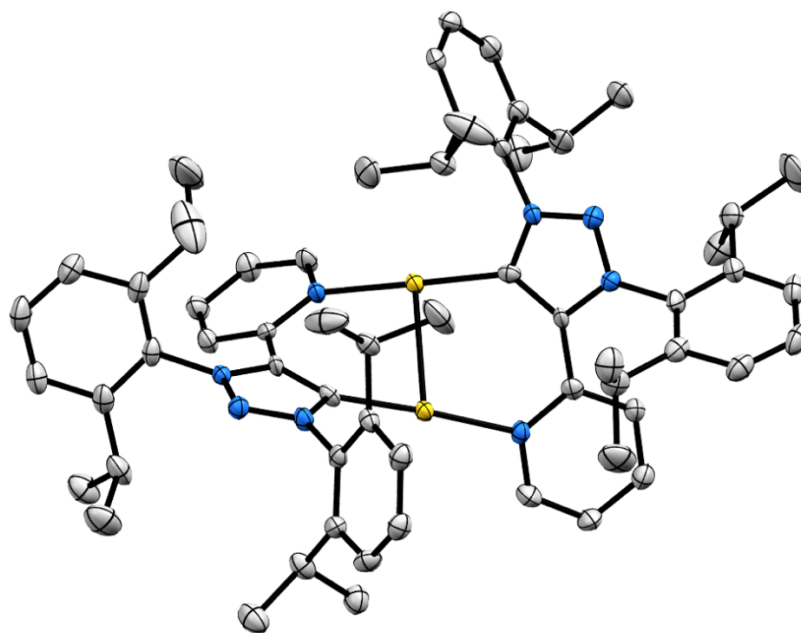
**Figure S90.** Crystal structure of **2b** (CCDC 2163610). Ellipsoids set at 50% probability; H atoms and solvent molecules omitted for clarity.

**Table S8.** Crystallographic parameters for **2b**.

<b>Chemical formula</b>	C <sub>32</sub> H <sub>42</sub> AuClN <sub>5</sub> O <sub>0.46</sub>	
<b>Formula weight</b>	736.44 g/mol	
<b>Temperature</b>	100(2) K	
<b>Wavelength</b>	0.71076 Å	
<b>Crystal size</b>	0.080 x 0.130 x 0.140 mm	
<b>Crystal system</b>	Triclinic	
<b>Space group</b>	P -1	
<b>Unit cell dimensions</b>	a = 9.426(7) Å	α = 108.17(2)°
	b = 12.481(9) Å	β = 91.20(3)°
	c = 15.289(12) Å	γ = 110.83(2)°
<b>Volume</b>	1580.(2) Å <sup>3</sup>	
<b>Density (calculated)</b>	1.548 g/cm <sup>3</sup>	
<b>Absorption coefficient</b>	4.771 mm <sup>-1</sup>	
<b>Final R indices</b>	8553 data; I > 2σ(I)	R1 = 0.0340, wR2 = 0.0740
	All data	R1 = 0.0482, wR2 = 0.0854

A colorless prism-like specimen of C<sub>32</sub>H<sub>42</sub>AuClN<sub>5</sub>O<sub>0.46</sub>, approximate dimensions 0.080 mm x 0.130 mm x 0.140 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a D8 QUEST ECO three-circle diffractometer system equipped with a Ceramic x-ray tube (Mo Kα, λ = 0.71076 Å) and a doubly curved silicon crystal Bruker Triumph monochromator. A total of 1634 frames were collected. The total exposure time was 2.27 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 172440 reflections to a maximum θ angle of 30.74° (0.70 Å resolution), of which 9738 were independent (average redundancy 17.708, completeness = 98.9%, R<sub>int</sub> = 7.14%, R<sub>sig</sub> = 2.66%) and 8553 (87.83%) were greater than 2σ(F<sup>2</sup>). The final cell constants of  $\underline{a}$  = 9.426(7) Å,  $\underline{b}$  = 12.481(9) Å,  $\underline{c}$  = 15.289(12) Å, α = 108.17(2)°, β = 91.20(3)°, γ = 110.83(2)°, volume = 1580.(2) Å<sup>3</sup>, are based upon the refinement of the XYZ-centroids of 9895 reflections above 20 σ(I) with 5.389° < 2θ < 59.94°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.795. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.5929 and 0.7461. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P -1, with Z = 2 for the formula unit, C<sub>32</sub>H<sub>42</sub>AuClN<sub>5</sub>O<sub>0.46</sub>. The final anisotropic full-matrix least-squares refinement on F<sup>2</sup> with 366 variables converged at R1 = 3.40%, for the observed data and wR2 = 8.54% for all data. The goodness-of-fit was 1.185. The largest peak in the final difference electron density synthesis was 4.477 e<sup>-</sup>/Å<sup>3</sup> and the largest hole was -2.675 e<sup>-</sup>/Å<sup>3</sup> with an RMS deviation of 0.167 e<sup>-</sup>/Å<sup>3</sup>. On the basis of the final model, the calculated density was 1.548 g/cm<sup>3</sup> and F(000), 737 e<sup>-</sup>.

### 9.3 Complex 3a



**Figure S91.** Crystal structure of **3a** (CCDC 2163617). Ellipsoids set at 50% probability; H atoms,  $\text{SbF}_6^-$  anions and solvent molecules are omitted for clarity.

**Table S9.** Crystallographic parameters for **3a**.

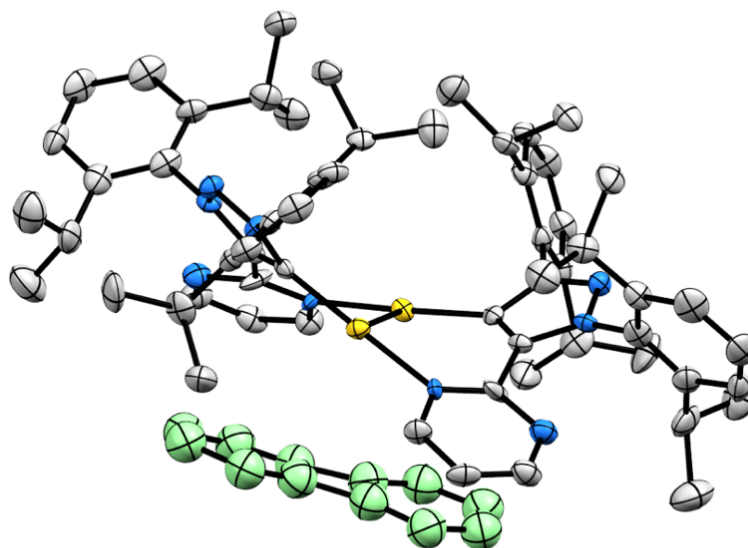
<b>Chemical formula</b>	$\text{C}_{67}\text{H}_{88}\text{Au}_2\text{Cl}_2\text{F}_{12}\text{N}_8\text{OSb}_2$	
<b>Formula weight</b>	1957.78 g/mol	
<b>Temperature</b>	100(2) K	
<b>Wavelength</b>	0.71073 Å	
<b>Crystal size</b>	0.040 x 0.250 x 0.280 mm	
<b>Crystal system</b>	Monoclinic	
<b>Space group</b>	P 1 21/c 1	
<b>Unit cell dimensions</b>	$a = 16.5318(8)$ Å	$\alpha = 90^\circ$
	$b = 17.9336(8)$ Å	$\beta = 107.017(2)^\circ$
	$c = 25.9388(12)$ Å	$\gamma = 90^\circ$
<b>Volume</b>	7353.5(6) Å <sup>3</sup>	
<b>Density (calculated)</b>	1.768 g/cm <sup>3</sup>	
<b>Absorption coefficient</b>	4.854 mm <sup>-1</sup>	
<b>Final R indices</b>	13720 data; $I > 2\sigma(I)$	R1 = 0.0513, wR2 = 0.1039
	All data	R1 = 0.0745, wR2 = 0.1178

A colorless plate-like specimen of  $\text{C}_{67}\text{H}_{88}\text{Au}_2\text{Cl}_2\text{F}_{12}\text{N}_8\text{OSb}_2$ , approximate dimensions 0.040 mm x 0.250 mm x 0.280 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a D8 QUEST ECO three-circle diffractometer



system equipped with a Ceramic x-ray tube (Mo K $\alpha$ ,  $\lambda = 0.71073 \text{ \AA}$ ) and a doubly curved silicon crystal Bruker Triumph monochromator. A total of 1837 frames were collected. The total exposure time was 1.89 hours. The frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 387971 reflections to a maximum  $\theta$  angle of  $27.54^\circ$  ( $0.77 \text{ \AA}$  resolution), of which 16936 were independent (average redundancy 22.908, completeness = 99.8%,  $R_{\text{int}} = 9.55\%$ ,  $R_{\text{sig}} = 3.26\%$ ) and 13720 (81.01%) were greater than  $2\sigma(F^2)$ . The final cell constants of  $a = 16.5318(8) \text{ \AA}$ ,  $b = 17.9336(8) \text{ \AA}$ ,  $c = 25.9388(12) \text{ \AA}$ ,  $\beta = 107.017(2)^\circ$ , volume =  $7353.5(6) \text{ \AA}^3$ , are based upon the refinement of the XYZ-centroids of 9283 reflections above  $20 \sigma(I)$  with  $5.632^\circ < 2\theta < 54.95^\circ$ . Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.564. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.3430 and 0.8300. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P 1 21/c 1, with  $Z = 4$  for the formula unit,  $C_{67}H_{88}Au_2Cl_2F_{12}N_8OSb_2$ . The final anisotropic full-matrix least-squares refinement on  $F^2$  with 859 variables converged at  $R1 = 5.13\%$ , for the observed data and  $wR2 = 11.78\%$  for all data. The goodness-of-fit was 1.242. The largest peak in the final difference electron density synthesis was  $3.857 \text{ e}^-/\text{\AA}^3$  and the largest hole was  $-2.415 \text{ e}^-/\text{\AA}^3$  with an RMS deviation of  $0.214 \text{ e}^-/\text{\AA}^3$ . On the basis of the final model, the calculated density was  $1.768 \text{ g/cm}^3$  and  $F(000)$ , 3824  $e^-$ .

#### 9.4 Complex **3b**·biphenylene



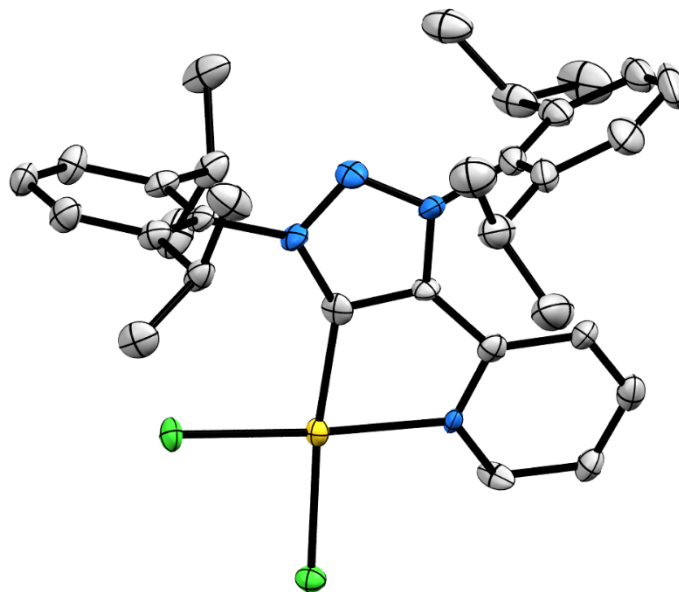
**Figure S92.** Crystal structure of **3b**·biphenylene (CCDC 2163613). Ellipsoids set at 50% probability; H atoms and  $SbF_6^-$  anions omitted for clarity. One molecule of biphenylene (in green) co-crystallized with one molecule of the dimeric Au(I) complex.

**Table S10.** Crystallographic parameters for **3b·biphenylene**.

<b>Chemical formula</b>	C <sub>72</sub> H <sub>82</sub> Au <sub>2</sub> F <sub>12</sub> N <sub>10</sub> Sb <sub>2</sub>	
<b>Formula weight</b>	1952.90 g/mol	
<b>Temperature</b>	100(2) K	
<b>Wavelength</b>	0.71073 Å	
<b>Crystal size</b>	0.060 x 0.180 x 0.230 mm	
<b>Crystal system</b>	Orthorhombic	
<b>Space group</b>	P b c n	
<b>Unit cell dimensions</b>	a = 25.668(9) Å	α = 90°
	b = 11.721(4) Å	β = 90°
	c = 25.249(9) Å	γ = 90°
<b>Volume</b>	7596.(5) Å <sup>3</sup>	
<b>Density (calculated)</b>	1.708 g/cm <sup>3</sup>	
<b>Absorption coefficient</b>	4.630 mm <sup>-1</sup>	
<b>Final R indices</b>	6113 data; I>2σ(I)	R1 = 0.0652, wR2 = 0.1282
	All data	R1 = 0.1075, wR2 = 0.1510

A yellow plate-like specimen of C<sub>72</sub>H<sub>82</sub>Au<sub>2</sub>F<sub>12</sub>N<sub>10</sub>Sb<sub>2</sub>, approximate dimensions 0.060 mm x 0.180 mm x 0.230 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a D8 QUEST ECO three-circle diffractometer system equipped with a Ceramic x-ray tube (Mo Kα, λ = 0.71073 Å) and a doubly curved silicon crystal Bruker Triumph monochromator. A total of 1107 frames were collected. The total exposure time was 1.54 hours. The frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. The integration of the data using an orthorhombic unit cell yielded a total of 330522 reflections to a maximum θ angle of 27.36° (0.77 Å resolution), of which 8574 were independent (average redundancy 38.549, completeness = 99.7%, R<sub>int</sub> = 13.94%, R<sub>sig</sub> = 3.73%) and 6113 (71.30%) were greater than 2σ(F<sup>2</sup>). The final cell constants of a = 25.668(9) Å, b = 11.721(4) Å, c = 25.249(9) Å, volume = 7596.(5) Å<sup>3</sup>, are based upon the refinement of the XYZ-centroids of 274 reflections above 20 σ(I) with 5.129° < 2θ < 34.22°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.706. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.4160 and 0.7690. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P b c n, with Z = 4 for the formula unit, C<sub>72</sub>H<sub>82</sub>Au<sub>2</sub>F<sub>12</sub>N<sub>10</sub>Sb<sub>2</sub>. The final anisotropic full-matrix least-squares refinement on F<sup>2</sup> with 496 variables converged at R1 = 6.52%, for the observed data and wR2 = 15.10% for all data. The goodness-of-fit was 1.243. The largest peak in the final difference electron density synthesis was 2.851 e<sup>-</sup>/Å<sup>3</sup> and the largest hole was -2.625 e<sup>-</sup>/Å<sup>3</sup> with an RMS deviation of 0.229 e<sup>-</sup>/Å<sup>3</sup>. On the basis of the final model, the calculated density was 1.708 g/cm<sup>3</sup> and F(000), 3808 e<sup>-</sup>.

## 9.5 Complex 4a-Cl



**Figure S93.** Crystal structure of **4a-Cl** (CCDC 2613611). Ellipsoids set at 50% probability; H atoms,  $\text{SbF}_6^-$  anion and solvent molecules are omitted for clarity.

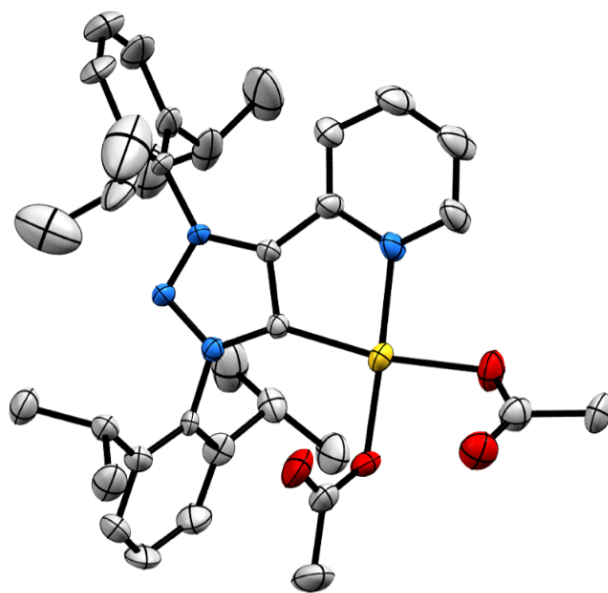
**Table S11.** Crystallographic parameters for **4a-Cl**.

<b>Chemical formula</b>	$\text{C}_{35}\text{H}_{50}\text{AuCl}_2\text{F}_6\text{N}_4\text{O}_2\text{Sb}$	
<b>Formula weight</b>	1062.40 g/mol	
<b>Temperature</b>	100(2) K	
<b>Wavelength</b>	0.71076 Å	
<b>Crystal size</b>	0.180 x 0.180 x 0.500 mm	
<b>Crystal system</b>	Triclinic	
<b>Space group</b>	P -1	
<b>Unit cell dimensions</b>	$a = 12.5020(6)$ Å	$\alpha = 83.846(2)^\circ$
	$b = 15.3475(8)$ Å	$\beta = 81.645(2)^\circ$
	$c = 22.3529(11)$ Å	$\gamma = 79.159(2)^\circ$
<b>Volume</b>	$4153.6(4)$ Å <sup>3</sup>	
<b>Density (calculated)</b>	1.699 g/cm <sup>3</sup>	
<b>Absorption coefficient</b>	4.368 mm <sup>-1</sup>	
<b>Final R indices</b>	17621 data; $I > 2\sigma(I)$	R1 = 0.0586, wR2 = 0.1292
	All data	R1 = 0.0762, wR2 = 0.1402

A yellow plate-like specimen of  $\text{C}_{35}\text{H}_{50}\text{AuCl}_2\text{F}_6\text{N}_4\text{O}_2\text{Sb}$ , approximate dimensions 0.180 mm x 0.180 mm x 0.500 mm, was used for the X-ray crystallographic analysis. The X-

ray intensity data were measured on a D8 QUEST ECO three-circle diffractometer system equipped with a Ceramic x-ray tube (Mo K $\alpha$ ,  $\lambda = 0.71076 \text{ \AA}$ ) and a doubly curved silicon crystal Bruker Triumph monochromator. A total of 2489 frames were collected. The total exposure time was 2.77 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 253080 reflections to a maximum  $\theta$  angle of  $28.38^\circ$  ( $0.75 \text{ \AA}$  resolution), of which 20753 were independent (average redundancy 12.195, completeness = 99.7%,  $R_{\text{int}} = 6.64\%$ ,  $R_{\text{sig}} = 3.14\%$ ) and 17621 (84.91%) were greater than  $2\sigma(F^2)$ . The final cell constants of  $a = 12.5020(6) \text{ \AA}$ ,  $b = 15.3475(8) \text{ \AA}$ ,  $c = 22.3529(11) \text{ \AA}$ ,  $\alpha = 83.846(2)^\circ$ ,  $\beta = 81.645(2)^\circ$ ,  $\gamma = 79.159(2)^\circ$ , volume =  $4153.6(4) \text{ \AA}^3$ , are based upon the refinement of the XYZ-centroids of 9298 reflections above  $20 \sigma(I)$  with  $6.073^\circ < 2\theta < 56.49^\circ$ . Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.794. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.4789 and 0.6035. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P  $-1$ , with  $Z = 4$  for the formula unit,  $\text{C}_{35}\text{H}_{50}\text{AuCl}_2\text{F}_6\text{N}_4\text{O}_2\text{Sb}$ . The final anisotropic full-matrix least-squares refinement on  $F^2$  with 933 variables converged at  $R1 = 5.86\%$ , for the observed data and  $wR2 = 14.02\%$  for all data. The goodness-of-fit was 1.236. The largest peak in the final difference electron density synthesis was  $4.225 \text{ e}^-/\text{\AA}^3$  and the largest hole was  $-3.184 \text{ e}^-/\text{\AA}^3$  with an RMS deviation of  $0.224 \text{ e}^-/\text{\AA}^3$ . On the basis of the final model, the calculated density was  $1.699 \text{ g/cm}^3$  and  $F(000)$ , 2088  $e^-$ .

## 9.6 Complex 4a-OAc



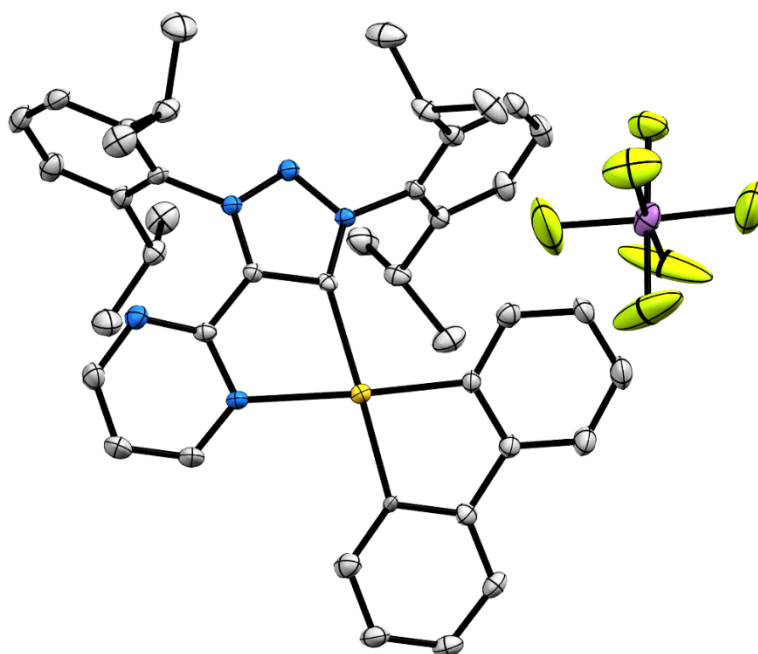
**Figure S94.** Crystal structure of **4a-OAc** (CCDC 2163608). Ellipsoids set at 50% probability; H atoms,  $\text{SbF}_6^-$  anion and solvent molecules are omitted for clarity.

**Table S12.** Crystallographic parameters for **4a-OAc**.

<b>Chemical formula</b>	C <sub>35</sub> H <sub>48</sub> AuF <sub>6</sub> N <sub>4</sub> O <sub>6</sub> Sb	
<b>Formula weight</b>	1053.49 g/mol	
<b>Temperature</b>	100(2) K	
<b>Wavelength</b>	0.71076 Å	
<b>Crystal size</b>	0.250 x 0.400 x 0.550 mm	
<b>Crystal system</b>	Triclinic	
<b>Space group</b>	P -1	
<b>Unit cell dimensions</b>	a = 11.63(4) Å	α = 76.35(10)°
	b = 12.52(5) Å	β = 72.58(7)°
	c = 15.71(6) Å	γ = 65.54(8)°
<b>Volume</b>	1970.(13) Å <sup>3</sup>	
<b>Density (calculated)</b>	1.776 g/cm <sup>3</sup>	
<b>Absorption coefficient</b>	4.480 mm <sup>-1</sup>	
<b>Final R indices</b>	8205 data; I>2σ(I)	R1 = 0.0894, wR2 = 0.2113
	All data	R1 = 0.1121, wR2 = 0.2361

A yellow block-like specimen of C<sub>35</sub>H<sub>48</sub>AuF<sub>6</sub>N<sub>4</sub>O<sub>6</sub>Sb, approximate dimensions 0.250 mm x 0.400 mm x 0.550 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a D8 QUEST ECO three-circle diffractometer system equipped with a Ceramic x-ray tube (Mo Kα, λ = 0.71076 Å) and a doubly curved silicon crystal Bruker Triumph monochromator. A total of 1206 frames were collected. The total exposure time was 2.68 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 86475 reflections to a maximum θ angle of 28.35° (0.75 Å resolution), of which 9804 were independent (average redundancy 8.820, completeness = 99.6%, R<sub>int</sub> = 4.12%, R<sub>sig</sub> = 2.38%) and 8205 (83.69%) were greater than 2σ(F<sup>2</sup>). The final cell constants of  $\underline{a}$  = 11.63(4) Å,  $\underline{b}$  = 12.52(5) Å,  $\underline{c}$  = 15.71(6) Å, α = 76.35(10)°, β = 72.58(7)°, γ = 65.54(8)°, volume = 1970.(13) Å<sup>3</sup>, are based upon the refinement of the XYZ-centroids of 9316 reflections above 20 σ(I) with 5.744° < 2θ < 56.54°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.592. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.4415 and 0.7457. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P -1, with Z = 2 for the formula unit, C<sub>35</sub>H<sub>48</sub>AuF<sub>6</sub>N<sub>4</sub>O<sub>6</sub>Sb. The final anisotropic full-matrix least-squares refinement on F<sup>2</sup> with 478 variables converged at R1 = 8.94%, for the observed data and wR2 = 23.61% for all data. The goodness-of-fit was 1.062. The largest peak in the final difference electron density synthesis was 10.949 e<sup>-</sup>/Å<sup>3</sup> and the largest hole was -6.868 e<sup>-</sup>/Å<sup>3</sup> with an RMS deviation of 0.335 e<sup>-</sup>/Å<sup>3</sup>. On the basis of the final model, the calculated density was 1.776 g/cm<sup>3</sup> and F(000), 1036 e<sup>-</sup>.

## 9.7 Complex 5b



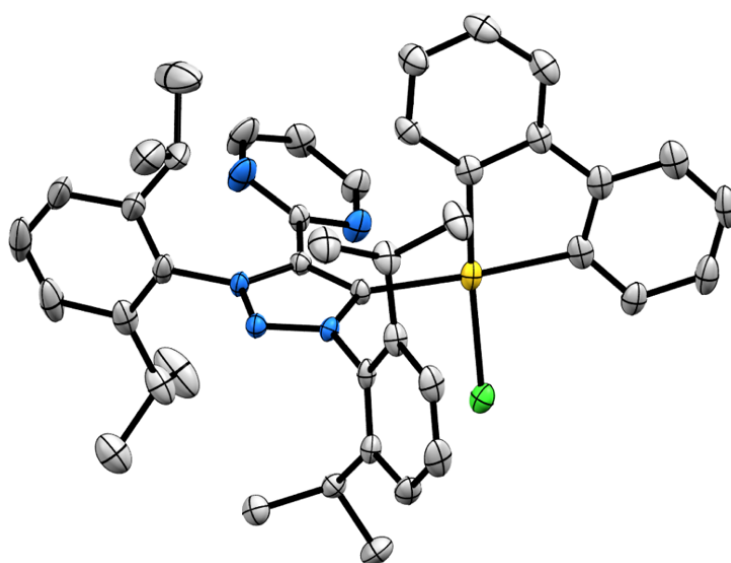
**Figure S95.** Crystal structure of **5b** (CCDC 2163614). Ellipsoids set at 50% probability; H atoms removed for clarity.

**Table S13.** Crystallographic parameters for **5b**.

<b>Chemical formula</b>	C <sub>42</sub> H <sub>45</sub> AuF <sub>6</sub> N <sub>5</sub> Sb	
<b>Formula weight</b>	1052.54 g/mol	
<b>Temperature</b>	100(2) K	
<b>Wavelength</b>	0.71073 Å	
<b>Crystal size</b>	0.060 x 0.070 x 0.400 mm	
<b>Crystal system</b>	Monoclinic	
<b>Space group</b>	P 1 21/n 1	
<b>Unit cell dimensions</b>	a = 17.0009(7) Å	α = 90°
	b = 11.7830(5) Å	β = 98.260(2)°
	c = 19.9923(8) Å	γ = 90°
<b>Volume</b>	3963.3(3) Å <sup>3</sup>	
<b>Density (calculated)</b>	1.764 g/cm <sup>3</sup>	
<b>Absorption coefficient</b>	4.445 mm <sup>-1</sup>	
<b>Final R indices</b>	9697 data; I > 2σ(I)	R1 = 0.0478, wR2 = 0.1097
	All data	R1 = 0.0642, wR2 = 0.1221

A yellow-green needle-like specimen of  $C_{42}H_{45}AuF_6N_5Sb$ , approximate dimensions 0.060 mm x 0.070 mm x 0.400 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a D8 QUEST ECO three-circle diffractometer system equipped with a Ceramic x-ray tube (Mo  $K\alpha$ ,  $\lambda = 0.71073 \text{ \AA}$ ) and a doubly curved silicon crystal Bruker Triumph monochromator. A total of 1507 frames were collected. The total exposure time was 3.74 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 261601 reflections to a maximum  $\theta$  angle of  $30.11^\circ$  ( $0.71 \text{ \AA}$  resolution), of which 11643 were independent (average redundancy 22.469, completeness = 99.7%,  $R_{\text{int}} = 7.53\%$ ,  $R_{\text{sig}} = 2.75\%$ ) and 9697 (83.29%) were greater than  $2\sigma(F^2)$ . The final cell constants of  $a = 17.0009(7) \text{ \AA}$ ,  $b = 11.7830(5) \text{ \AA}$ ,  $c = 19.9923(8) \text{ \AA}$ ,  $\beta = 98.260(2)^\circ$ , volume =  $3963.3(3) \text{ \AA}^3$ , are based upon the refinement of the XYZ-centroids of 9273 reflections above  $20 \sigma(I)$  with  $5.950^\circ < 2\theta < 60.08^\circ$ . Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.629. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.2690 and 0.7760. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group  $P 1 21/n 1$ , with  $Z = 4$  for the formula unit,  $C_{42}H_{45}AuF_6N_5Sb$ . The final anisotropic full-matrix least-squares refinement on  $F^2$  with 504 variables converged at  $R1 = 4.78\%$ , for the observed data and  $wR2 = 12.21\%$  for all data. The goodness-of-fit was 1.063. The largest peak in the final difference electron density synthesis was  $9.167 \text{ e}^-/\text{\AA}^3$  and the largest hole was  $-4.458 \text{ e}^-/\text{\AA}^3$  with an RMS deviation of  $0.221 \text{ e}^-/\text{\AA}^3$ . On the basis of the final model, the calculated density was  $1.764 \text{ g/cm}^3$  and  $F(000)$ , 2064  $e^-$ .

## 9.8 Complex 6b



**Figure S96.** Crystal structure of **6b** (CCDC 2163615). Ellipsoids set at 50% probability; H atoms removed for clarity.

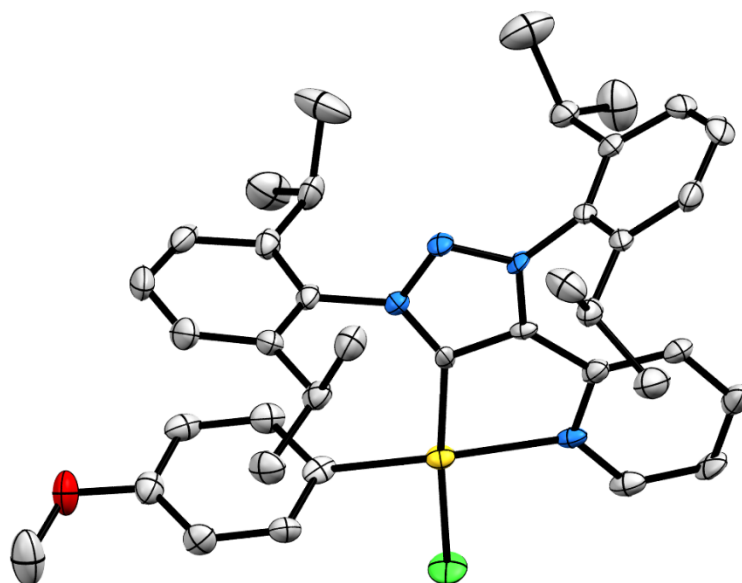
**Table S14.** Crystallographic parameters for **6b**.

<b>Chemical formula</b>	C <sub>46</sub> H <sub>55</sub> AuClN <sub>5</sub> O	
<b>Formula weight</b>	926.36 g/mol	
<b>Temperature</b>	100(2) K	
<b>Wavelength</b>	0.71076 Å	
<b>Crystal size</b>	0.110 x 0.110 x 0.150 mm	
<b>Crystal system</b>	Triclinic	
<b>Space group</b>	P -1	
<b>Unit cell dimensions</b>	a = 12.25(2) Å	α = 89.58(3)°
	b = 15.50(2) Å	β = 84.70(4)°
	c = 23.22(4) Å	γ = 85.16(4)°
<b>Volume</b>	4374.(12) Å <sup>3</sup>	
<b>Density (calculated)</b>	1.406 g/cm <sup>3</sup>	
<b>Absorption coefficient</b>	3.462 mm <sup>-1</sup>	
<b>Final R indices</b>	16770 data; I>2σ(I)	R1 = 0.0509, wR2 = 0.1007
	All data	R1 = 0.0801, wR2 = 0.1158

A colorless prism-like specimen of C<sub>46</sub>H<sub>55</sub>AuClN<sub>5</sub>O, approximate dimensions 0.110 mm x 0.110 mm x 0.150 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a D8 QUEST ECO three-circle diffractometer system equipped with a Ceramic x-ray tube (Mo Kα, λ = 0.71076 Å) and a doubly curved silicon crystal Bruker Triumph monochromator. A total of 1467 frames were collected. The total exposure time was 3.26 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 285667 reflections to a maximum θ angle of 28.32° (0.75 Å resolution), of which 21662 were independent (average redundancy 13.187, completeness = 99.2%, R<sub>int</sub> = 8.17%, R<sub>sig</sub> = 3.95%) and 16770 (77.42%) were greater than 2σ(F<sup>2</sup>). The final cell constants of  $\underline{a}$  = 12.25(2) Å,  $\underline{b}$  = 15.50(2) Å,  $\underline{c}$  = 23.22(4) Å, α = 89.58(3)°, β = 84.70(4)°, γ = 85.16(4)°, volume = 4374.(12) Å<sup>3</sup>, are based upon the refinement of the XYZ-centroids of 9795 reflections above 20 σ(I) with 5.578° < 2θ < 56.18°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.717. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.5345 and 0.7457. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P -1, with Z = 4 for the formula unit, C<sub>46</sub>H<sub>55</sub>AuClN<sub>5</sub>O. The final anisotropic full-matrix least-squares refinement on F<sup>2</sup> with 993 variables converged at R1 = 5.09%, for the observed data and wR2 = 11.58% for all data. The goodness-of-fit was 1.271. The largest peak in the final difference electron density synthesis was 4.528 e<sup>-</sup>/Å<sup>3</sup> and the largest hole was -3.736 e<sup>-</sup>/Å<sup>3</sup> with an RMS deviation of 0.170 e<sup>-</sup>/Å<sup>3</sup>. On the basis of the final model, the calculated density was 1.406 g/cm<sup>3</sup> and F(000), 1880 e<sup>-</sup>.



## 9.9 Complex *cis-7a-Cl*



**Figure S97.** Crystal structure of *cis-7a-Cl* (CCDC 2176932). Ellipsoids set at 50% probability; H atoms,  $\text{BF}_4^-$  anion and solvent molecules are omitted for clarity.

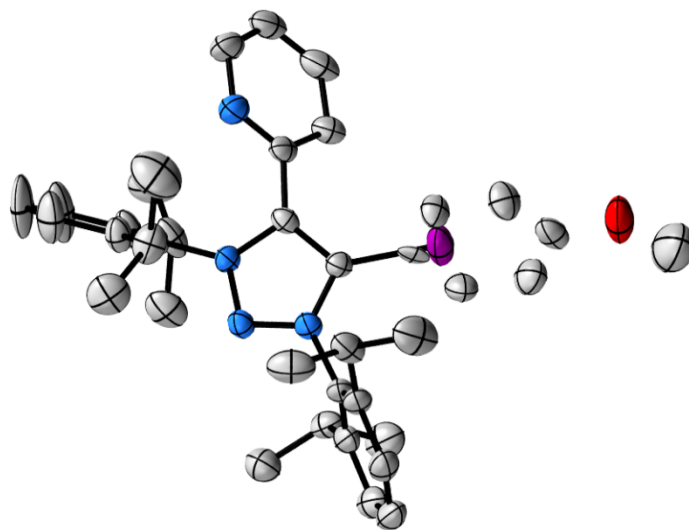
**Table S15.** Crystallographic parameters for *cis-7a-Cl*. The chemical formula is given for 4 molecules of complex *cis-7a-Cl* and 5 molecules of N,N-dimethylformamide.

<b>Chemical formula</b>	$\text{C}_{167}\text{H}_{215}\text{Au}_4\text{B}_4\text{Cl}_4\text{F}_{16}\text{N}_{21}\text{O}_9$	
<b>Formula weight</b>	3937.49 g/mol	
<b>Temperature</b>	100(2) K	
<b>Wavelength</b>	0.71073 Å	
<b>Crystal size</b>	0.040 x 0.040 x 0.200 mm	
<b>Crystal system</b>	Triclinic	
<b>Space group</b>	P -1	
<b>Unit cell dimensions</b>	$a = 16.4149(8) \text{ \AA}$	$\alpha = 64.1050(10)^\circ$
	$b = 23.5323(12) \text{ \AA}$	$\beta = 80.992(2)^\circ$
	$c = 24.8306(13) \text{ \AA}$	$\gamma = 81.2460(10)^\circ$
<b>Volume</b>	$8484.1(7) \text{ \AA}^3$	
<b>Density (calculated)</b>	1.541 g/cm <sup>3</sup>	
<b>Absorption coefficient</b>	3.591 mm <sup>-1</sup>	
<b>Final R indices</b>	27208 data; $I > 2\sigma(I)$	R1 = 0.0658, wR2 = 0.1318
	All data	R1 = 0.1132, wR2 = 0.1554

A colorless plate-like specimen of  $\text{C}_{167}\text{H}_{215}\text{Au}_4\text{B}_4\text{Cl}_4\text{F}_{16}\text{N}_{21}\text{O}_9$ , approximate dimensions 0.040 mm x 0.040 mm x 0.200 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a D8 QUEST ECO three-circle diffractometer

system equipped with a Ceramic x-ray tube (Mo K $\alpha$ ,  $\lambda = 0.71073 \text{ \AA}$ ) and a doubly curved silicon crystal Bruker Triumph monochromator. A total of 1043 frames were collected. The total exposure time was 8.69 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 512292 reflections to a maximum  $\theta$  angle of  $27.61^\circ$  ( $0.77 \text{ \AA}$  resolution), of which 39296 were independent (average redundancy 13.037, completeness = 99.7%,  $R_{\text{int}} = 14.35\%$ ,  $R_{\text{sig}} = 7.00\%$ ) and 27208 (69.24%) were greater than  $2\sigma(F^2)$ . The final cell constants of  $a = 16.4149(8) \text{ \AA}$ ,  $b = 23.5323(12) \text{ \AA}$ ,  $c = 24.8306(13) \text{ \AA}$ ,  $\alpha = 64.1050(10)^\circ$ ,  $\beta = 80.992(2)^\circ$ ,  $\gamma = 81.2460(10)^\circ$ , volume =  $8484.1(7) \text{ \AA}^3$ , are based upon the refinement of the XYZ-centroids of 9838 reflections above  $20 \sigma(I)$  with  $5.770^\circ < 2\theta < 53.65^\circ$ . Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.802. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.5340 and 0.8700. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P -1, with  $Z = 2$  for the formula unit,  $C_{167}H_{215}Au_4B_4Cl_4F_{16}N_{21}O_9$ . The final anisotropic full-matrix least-squares refinement on  $F^2$  with 2037 variables converged at  $R1 = 6.58\%$ , for the observed data and  $wR2 = 15.54\%$  for all data. The goodness-of-fit was 1.098. The largest peak in the final difference electron density synthesis was  $2.818 \text{ e}^-/\text{\AA}^3$  and the largest hole was  $-4.916 \text{ e}^-/\text{\AA}^3$  with an RMS deviation of  $0.200 \text{ e}^-/\text{\AA}^3$ . On the basis of the final model, the calculated density was  $1.541 \text{ g/cm}^3$  and  $F(000)$ , 3968  $e^-$ .

### 9.10 Compounds 8a-OMe and 9a



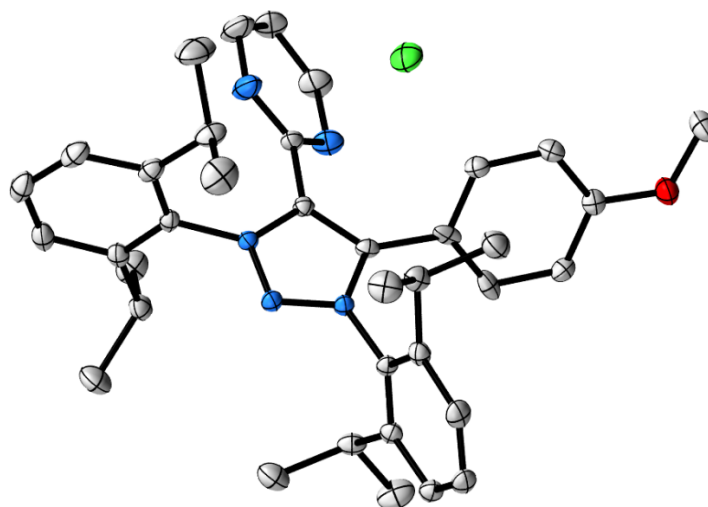
**Figure S98.** Crystal structure of **8a-OMe** co-crystallized with a minor amount of compound **9a** in a 0.89:0.11 ratio (CCDC 2163612). Ellipsoids set at 50% probability; H atoms and  $SbF_6^-$  anion removed for clarity.

**Table S16.** Crystallographic parameters for the co-crystallization of **8a-OMe** and **9a** in a 0.89:0.11 ratio.

<b>Chemical formula</b>	C <sub>37.26</sub> H <sub>44.26</sub> F <sub>6</sub> I <sub>0.11</sub> N <sub>4</sub> O <sub>0.89</sub> Sb	
<b>Formula weight</b>	811.62 g/mol	
<b>Temperature</b>	100(2) K	
<b>Wavelength</b>	0.71076 Å	
<b>Crystal size</b>	0.210 x 0.220 x 0.240 mm	
<b>Crystal system</b>	Monoclinic	
<b>Space group</b>	P 1 21/n 1	
<b>Unit cell dimensions</b>	a = 12.29(4) Å	α = 90°
	b = 16.44(5) Å	β = 101.35(6)°
	c = 19.22(6) Å	γ = 90°
<b>Volume</b>	3807.(19) Å <sup>3</sup>	
<b>Density (calculated)</b>	1.416 g/cm <sup>3</sup>	
<b>Absorption coefficient</b>	0.873 mm <sup>-1</sup>	
<b>Final R indices</b>	4525 data; I>2σ(I)	R1 = 0.0680, wR2 = 0.1365
	All data	R1 = 0.0892, wR2 = 0.1468

A colorless prism-like specimen of C<sub>37.26</sub>H<sub>44.26</sub>F<sub>6</sub>I<sub>0.11</sub>N<sub>4</sub>O<sub>0.89</sub>Sb, approximate dimensions 0.210 mm x 0.220 mm x 0.240 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a D8 QUEST ECO three-circle diffractometer system equipped with a Ceramic x-ray tube (Mo Kα, λ = 0.71076 Å) and a doubly curved silicon crystal Bruker Triumph monochromator. A total of 1006 frames were collected. The total exposure time was 8.38 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 69569 reflections to a maximum θ angle of 23.61° (0.89 Å resolution), of which 5671 were independent (average redundancy 12.268, completeness = 99.1%, R<sub>int</sub> = 7.44%, R<sub>sig</sub> = 3.54%) and 4525 (79.79%) were greater than 2σ(F<sup>2</sup>). The final cell constants of a = 12.29(4) Å, b = 16.44(5) Å, c = 19.22(6) Å, β = 101.35(6)°, volume = 3807.(19) Å<sup>3</sup>, are based upon the refinement of the XYZ-centroids of 9982 reflections above 20 σ(I) with 6.003° < 2θ < 45.68°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.866. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.6449 and 0.7449. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P 1 21/n 1, with Z = 4 for the formula unit, C<sub>37.26</sub>H<sub>44.26</sub>F<sub>6</sub>I<sub>0.11</sub>N<sub>4</sub>O<sub>0.89</sub>Sb. The final anisotropic full-matrix least-squares refinement on F<sup>2</sup> with 458 variables converged at R1 = 6.80%, for the observed data and wR2 = 14.68% for all data. The goodness-of-fit was 1.185. The largest peak in the final difference electron density synthesis was 1.114 e<sup>-</sup>/Å<sup>3</sup> and the largest hole was -1.089 e<sup>-</sup>/Å<sup>3</sup> with an RMS deviation of 0.090 e<sup>-</sup>/Å<sup>3</sup>. On the basis of the final model, the calculated density was 1.416 g/cm<sup>3</sup> and F(000), 1654 e<sup>-</sup>.

## 9.11 Compound 8b-OMe



**Figure S99.** Crystal structure of **8b-OMe** (CCDC 2163616). Ellipsoids set at 50% probability; H atoms removed for clarity.

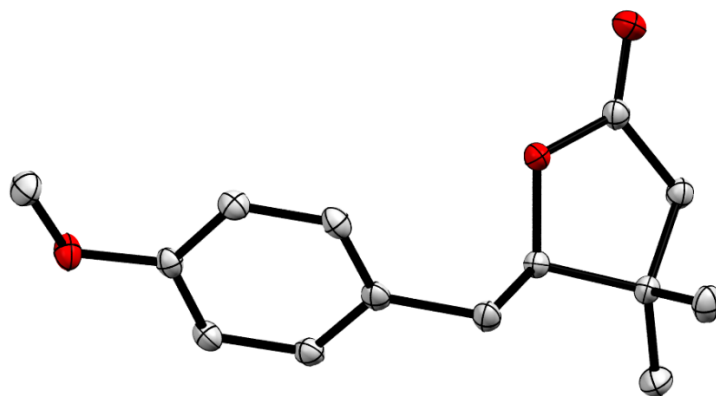
**Table S17.** Crystallographic parameters for **8b-OMe**.

<b>Chemical formula</b>	C <sub>37</sub> H <sub>46</sub> ClN <sub>5</sub> O <sub>2</sub>	
<b>Formula weight</b>	628.24 g/mol	
<b>Temperature</b>	100(2) K	
<b>Wavelength</b>	0.71076 Å	
<b>Crystal size</b>	0.080 x 0.090 x 0.190 mm	
<b>Crystal system</b>	Monoclinic	
<b>Space group</b>	P 1 21/c 1	
<b>Unit cell dimensions</b>	a = 11.589(10) Å	α = 90°
	b = 11.486(9) Å	β = 97.78(2)°
	c = 26.60(3) Å	γ = 90°
<b>Volume</b>	3508.(5) Å <sup>3</sup>	
<b>Density (calculated)</b>	1.190 g/cm <sup>3</sup>	
<b>Absorption coefficient</b>	0.148 mm <sup>-1</sup>	
<b>Final R indices</b>	6967 data; I > 2σ(I)	R1 = 0.0602, wR2 = 0.1425
	All data	R1 = 0.0697, wR2 = 0.1481

A colorless prism-like specimen of C<sub>37</sub>H<sub>46</sub>ClN<sub>5</sub>O<sub>2</sub>, approximate dimensions 0.080 mm x 0.090 mm x 0.190 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a D8 QUEST ECO three-circle diffractometer system equipped with a Ceramic x-ray tube (Mo Kα, λ = 0.71076 Å) and a doubly curved silicon crystal Bruker Triumph monochromator. A total of 774 frames were collected. The total

exposure time was 17.20 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 107985 reflections to a maximum  $\theta$  angle of  $27.50^\circ$  ( $0.77 \text{ \AA}$  resolution), of which 8030 were independent (average redundancy 13.448, completeness = 99.8%,  $R_{\text{int}} = 4.51\%$ ,  $R_{\text{sig}} = 2.04\%$ ) and 6967 (86.76%) were greater than  $2\sigma(F^2)$ . The final cell constants of  $a = 11.589(10) \text{ \AA}$ ,  $b = 11.486(9) \text{ \AA}$ ,  $c = 26.60(3) \text{ \AA}$ ,  $\beta = 97.78(2)^\circ$ , volume =  $3508.5 \text{ \AA}^3$ , are based upon the refinement of the XYZ-centroids of 9889 reflections above  $20 \sigma(I)$  with  $5.648^\circ < 2\theta < 56.59^\circ$ . Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.950. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9720 and 0.9880. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group  $P 1 21/c 1$ , with  $Z = 4$  for the formula unit,  $C_{37}H_{46}ClN_5O_2$ . The final anisotropic full-matrix least-squares refinement on  $F^2$  with 423 variables converged at  $R1 = 6.02\%$ , for the observed data and  $wR2 = 14.81\%$  for all data. The goodness-of-fit was 1.123. The largest peak in the final difference electron density synthesis was  $1.307 \text{ e}^-/\text{\AA}^3$  and the largest hole was  $-0.508 \text{ e}^-/\text{\AA}^3$  with an RMS deviation of  $0.058 \text{ e}^-/\text{\AA}^3$ . On the basis of the final model, the calculated density was  $1.190 \text{ g/cm}^3$  and  $F(000)$ , 1344  $e^-$ .

## 9.12 Compound 16



**Figure S100.** Crystal structure of **16** (CCDC 2163877). Ellipsoids set at 50% probability; H atoms removed for clarity.

**Table S18.** Crystallographic parameters for **16**.

<b>Chemical formula</b>	C <sub>14</sub> H <sub>18</sub> O <sub>3</sub>	
<b>Formula weight</b>	234.28 g/mol	
<b>Temperature</b>	100(2) K	
<b>Wavelength</b>	0.71073 Å	
<b>Crystal size</b>	0.370 x 0.370 x 0.450 mm	
<b>Crystal system</b>	Orthorhombic	
<b>Space group</b>	P 21 21 21	
<b>Unit cell dimensions</b>	a = 6.3989(2) Å	α = 90°
	b = 7.1432(2) Å	β = 90°
	c = 27.0217(7) Å	γ = 90°
<b>Volume</b>	1235.12(6) Å <sup>3</sup>	
<b>Density (calculated)</b>	1.260 g/cm <sup>3</sup>	
<b>Absorption coefficient</b>	0.087 mm <sup>-1</sup>	
<b>Final R indices</b>	3051 data; I>2σ(I)	R1 = 0.0282, wR2 = 0.0731
	All data	R1 = 0.0287, wR2 = 0.0736

A colorless prism-like specimen of C<sub>14</sub>H<sub>18</sub>O<sub>3</sub>, approximate dimensions 0.370 mm x 0.370 mm x 0.450 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a D8 QUEST ECO three-circle diffractometer system equipped with a Ceramic x-ray tube (Mo Kα, λ = 0.71073 Å) and a doubly curved silicon crystal Bruker Triumph monochromator. A total of 364 frames were collected. The total exposure time was 0.51 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using an orthorhombic unit cell yielded a total of 6921 reflections to a maximum θ angle of 28.50° (0.74 Å resolution), of which 3097 were independent (average redundancy 2.235, completeness = 98.8%, R<sub>int</sub> = 1.23%, R<sub>sig</sub> = 1.68%) and 3051 (98.51%) were greater than 2σ(F<sup>2</sup>). The final cell constants of  $\underline{a}$  = 6.3989(2) Å,  $\underline{b}$  = 7.1432(2) Å,  $\underline{c}$  = 27.0217(7) Å, volume = 1235.12(6) Å<sup>3</sup>, are based upon the refinement of the XYZ-centroids of 7019 reflections above 20 σ(I) with 5.899° < 2θ < 68.62°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.873. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9620 and 0.9680. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P 21 21 21, with Z = 4 for the formula unit, C<sub>14</sub>H<sub>18</sub>O<sub>3</sub>. The final anisotropic full-matrix least-squares refinement on F<sup>2</sup> with 157 variables converged at R1 = 2.82%, for the observed data and wR2 = 7.36% for all data. The goodness-of-fit was 1.063. The largest peak in the final difference electron density synthesis was 0.278 e<sup>-</sup>/Å<sup>3</sup> and the largest hole was -0.163 e<sup>-</sup>/Å<sup>3</sup> with an RMS deviation of 0.033 e<sup>-</sup>/Å<sup>3</sup>. On the basis of the final model, the calculated density was 1.260 g/cm<sup>3</sup> and F(000), 504 e<sup>-</sup>.

## 10. References

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