

# SYNTHESIS AND REACTIVITY OF N-HETEROCYCLIC GOLD (I) COMPLEXES



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# ABSTRACT

Several *N*-heterocyclic gold (I) complexes were synthesized featuring both the bis-(2,4,6-trimethylphenyl)imidazolium carbene (IMes) ligand and the bis-(1,3-diisopropylphenyl)imidazolium carbene (IPr) ligand. Complexes of the form LAuCl, LAuOtBu, and LAuPh (L = IMes, IPr) were synthesized and characterized using  $^1\text{H-NMR}$ . Two updated crystal structures of IMesAuPh and chloro(dimethylsulfide)gold(I) were established. The reaction between IMesAuPh and iodobenzene in deuterated benzene at 90°C and 110°C, using an internal standard (cyclooctane) was studied in detail. According to Johnson<sup>1</sup> *et al*, the reaction was novel of its kind by showing a complete new reactivity involving Au(I) species. The primary objective was to study the kinetics of this novel reaction. Surprisingly, additional investigation unfolded data which supported the likelihood of Au(0) catalysis where the NHC Au(I) species would serve as an intermediate in CC coupling. Observation of a purple coating on the Young tubes together with a very late formation of biphenyl supported Au(0) catalysis. At slightly lower reaction temperature (90°C), no observable amount of cross-coupling product could be observed, even after vastly prolonged reaction times. Additional control experiments using both a catalytic and stoichiometric additive of a palladium pincer complex (PCP-PdCl) yielded similar reactivity pattern as earlier reported, thus rendering biphenyl as in the gold(I)-only case accompanied by the simultaneous forming IMesAuI. Copper impurities is likely not affecting catalysis as different intermediates are observed compared to when Pd or non Pd experiments are run. Clearly, palladium sources may be a contributing factor in the formation of cross-coupling product. This new data identifies the pivotal need to run further control experiments, to exclude any involvement of palladium responsible for catalysis and not Au(0) by as well study the effect of any *in situ* Au(0) formation.

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*"Chemistry means the difference between poverty and starvation  
and the abundant life" (Robert Brent)*

# POPULAR SCIENTIFIC SUMMARY

Organometallics is a branch of chemistry focusing on developing new reactions using transition metals, e.g. iron, cobalt, gold, where common organic C-H bonds occur in combination with the metals. By using transition metals in chemistry, new products are accessible, which could otherwise not be produced using conventional chemistry. Additionally, selectivity, waste reduction, minimization of byproducts, shortened reaction time, or a lowering of the reaction temperature are only a few of the important features which transition metal catalyzed reactions may offer. Lower temperature implies that less energy is consumed, which is of great importance to the industry and has an impact on our environment. In conclusion, organometallics can be used in a way to improve life on this planet.

Organometallic chemistry also has many applications, e.g. in the formation of polymers such as plastics. Essentially every plastic which is used today is made from carbon-carbon single bonds, which in turn are formed in processes using transition metals. Other uses are in the production of agrochemicals, so that we can grow crops in the density we need to feed the growing global population. A relatively new application is organic light emitting diodes (OLEDs), which is now in use in cell phones, making the screens flexible. In future, this could possibly be used as a material on wallpapers to light up a room.

Gold is an example of a transition metal, it is denoted Au (*lat.* aurum). Elemental gold is found everywhere in our daily life. This form of gold has a low oxidation state Au(0), and does not easily transfer electrons. Elemental gold thus shows a low reactivity, and is difficult to use in the chemistry explained above. Instead, the two other important oxidation states of gold, namely gold(I) and gold (III) can be used. These species are much more reactive as they can take up electrons and be reduced to elemental gold, while something else gets oxidized (gives off electrons). In my work, I have used gold(I) species and studied different reactions, to obtain basic understanding of the reactivity of gold complexes. It is important to in depth study and understand this fundamental chemistry if we want to be able to construct new applications like the ones described above. The motivation for using gold in chemistry rather than e.g. platinum or rhodium, which are traditionally used, is surprisingly because gold is relatively inexpensive and abundant. Additionally, gold due to its large size offers a different set of properties and reactivity than other transition metals.

Supervisor: Dr. André Fleckhaus

Examensarbete 30 hp in Organometallic Chemistry , 2013

Institution for Chemistry: Centre for Analysis and Synthesis

# POPULÄRVETENSKAPLIG SAMMANFATTNING

Metallorganisk kemi är en gren av kemin som fokuserar på att utveckla nya reaktioner med hjälp av övergångsmetaller som t.ex. järn, kobolt och guld. Genom att använda övergångsmetaller i kemi är det möjligt att bilda nya reaktioner som man med konventionell organisk kemi inte kan få tillgång till. Dessutom är selektivitet, avfallsminskning, minimering av biprodukter, förkortad reaktionstid eller en sänkning av reaktionstemperaturen några exempel på viktiga egenskaper som övergångsmetallkatalyserade reaktioner kan erbjuda. Lägre temperatur innebär att mindre energi förbrukas vilket är av stor betydelse för industrin, vilket i sin tur naturligtvis påverkar vår miljö. Sammanfattningsvis kan metallorganisk kemi användas för att förbättra livet för människan.

Metallorganisk kemi har också många tillämpningar, t.ex. vid bildning av polymerer som plaster. I princip varje plast som används idag är tillverkad ur reaktioner som skapar kol-kol-enkelbindningar, och detta i processer som använder övergångsmetaller. Andra användningsområden är i produktionen av jordbrukskemikalier, så att vi kan odla grödor i den omfattning som behövs för att föda den växande globala befolkningen. En relativt ny applikation är organiska lysdioder (oLED), som nu är i användning i moderna mobiltelefoner och som gör skärmen flexibel. Inom kort skulle detta möjligen kunna användas som ett material för att bakgrundsbelysa ett helt rum genom att tapetsera med oLEDs.

Guld är ett exempel på en övergångsmetall och den betecknas Au (*lat.* aurum). Elementärt guld finns överallt i vårt dagliga liv, t.ex. i smycken. Denna form av guld har ett lågt oxidationstillstånd  $\text{Au}(0)$ , och byter inte gärna elektroner. Elementärt guld visar sålunda en låg reaktivitet och är svår att använda i den kemi som är beskriven ovan. Istället kan de två andra oxidationstillstånden hos guld, nämligen guld (I) och guld (III) nyttjas. Dessa former är mer reaktiva. I mitt arbete har jag skapat guld (I) komplex för att studera reaktiviteten och få en grundläggande kunskap kring deras kemi. Det är viktigt att på djupet studera och förstå denna grundläggande kemi om vi vill kunna bygga nya applikationer som de ovan nämnda. Anledningen att använda guld i kemi snarare än t.ex. platina eller rodium, som traditionellt används, är att guld är förvånansvärt billigt i jämförelse med rodium och platina samtidigt som det finns gott om guldreserver på jorden.

Handledare: André Fleckhaus

Examensarbete 30 hp i Metallorganisk kemi, 2013

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# INTRODUCTION

## 1.1 GENERAL PROPERTIES OF GOLD

Elemental gold (Au(0)) has been known to humanity thousands of years.<sup>2</sup> Surprisingly, only very few examples of chemistry involving gold catalysis have been demonstrated until recent years.<sup>1</sup> Note that stoichiometric gold chemistry has not had the same lack of interest. An interest to form elemental gold has been more important, than to actually investigate what can be made *using* gold.<sup>2</sup> Traditionally, this has most likely stemmed from the high price of gold or perhaps a misbelief that gold(I) or gold(III) species would show the same low reactivity as elemental gold. Nonetheless, chemist now use gold in catalysis mainly through two motivations; price and selectivity. Hasmi<sup>2</sup> reported in a recent review, the interest in gold catalyzed organic transformations has increased remarkably from 2005.

First, the main reason for using gold in catalysis is that specific and unique reactivity trends are attainable, a specificity for substrates specifically covering enynes has been reported.<sup>3</sup> The specificity may then result in high yielding and chemoselective organic transformations enabling new routes in synthetic chemistry. This reactivity could be attributed to the inherent properties of gold, such as the softness and its lanthanide contraction. The softness of the metal altogether make it highly interactive with pi-systems which is demonstrated by its rich cyclization chemistry.<sup>2</sup> In this project, gold(I) complexes are mainly used. Gold(I) has the electronic configuration  $[\text{Xe}]4f^{14}5d^{10}$  and is often called a soft metal.<sup>4</sup> These properties causes the Au(I) to interact most favorably with soft ligands containing sulfur or carbon.<sup>4</sup>

The second reason for using gold in catalysis is the price. By comparing prices per gram for palladium, platinum, rhodium, and gold, it is apparent that gold is comparatively less expensive than both rhodium and platinum.<sup>2,5</sup> Though, it is important to recall that the most expensive part of a homogenous catalyst often lies on the ligand and not the metal center.<sup>2</sup>

A few general remarks concerning gold is that only a few oxidation states are accessible when bound to a ligand; gold(0), gold(I) and gold(III). Without any coordinating ligand, and in aqueous solution, gold(I) species spontaneously lies in equilibrium to form gold(0) and gold(III) species.<sup>2</sup> A major advantage using gold in catalysis is that both gold(I) and gold(III) are diamagnetic, allowing reactions easily to be monitored on NMR.

## 1.2 CROSS-COUPLING REACTIONS INVOLVING GOLD

The idea of using gold in homogenous catalysis has grown dramatically during recent years.<sup>2</sup> One large but novel domain involves *N*-heterocyclic gold complexes of both gold(I) and gold(III). Especially gold (I) or gold(III) complexes bearing a sterically crowded ligand of the type *N*-heterocyclic carbenes has proven reliable for many reasons, such as rigidity, and its ease to chemically fine tune. These electron rich ligands increases the reactivity due to the trans effect.<sup>6,7</sup> *N*-heterocyclic carbenes primarily operates as sigma donors by pushing electron density to the metal center and stabilizing the gold cation.<sup>8,9</sup> Additionally, this creates a rather nucleophilic LAu-X bond depending on what X is and for which the relative basicity has been studied by Blum<sup>10</sup> and coworkers. *N*-heterocyclic carbene ligands have not only been showing interesting results in gold catalysis but has been pivotal for metathesis. One example is Grubbs catalyst responsible for metathesis, a branch which is claimed to be one of the most potent synthetic instruments in organic chemistry.<sup>11,6</sup>

The reaction between *N*-heterocyclic gold(I) aryl species and aryl halides for cross-couplings have been scarce until Johnson<sup>1</sup> *et al* demonstrated reactivity with IMeAuPh. However, DFT calculations showed that Au(III) had a significant barrier to the oxidative addition of phenyl iodide (Figure 0) to the metal centre which was also supported by their experimental data showing no Au(III) species. The study of mechanisms is an endeavouring task, and as modern techniques and applications develop, new mechanistic insight is attainable. Recently, many new findings have shown that recently believed Au(I) catalyzed reactions has in fact been catalyzed by trace impurities of palladium which at an early stage was difficult to detect. These cross-coupling discoveries have involved Suzuki, Sonogashira reactions.<sup>12</sup> It has had a remarkable impact on the question what actually catalyzes a given reaction.

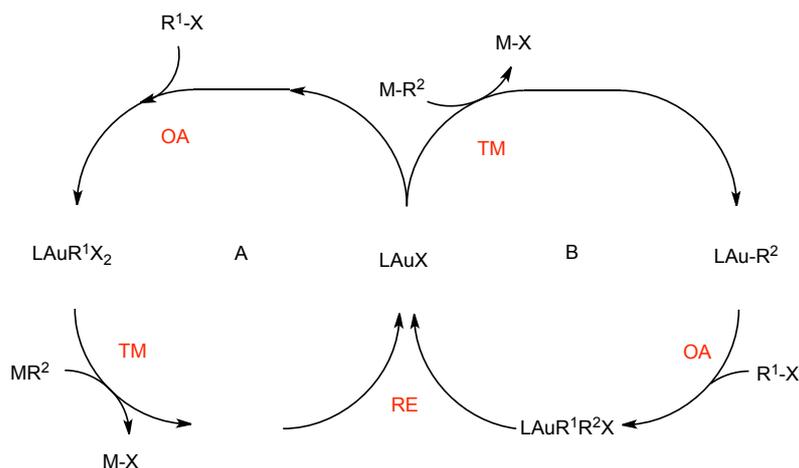
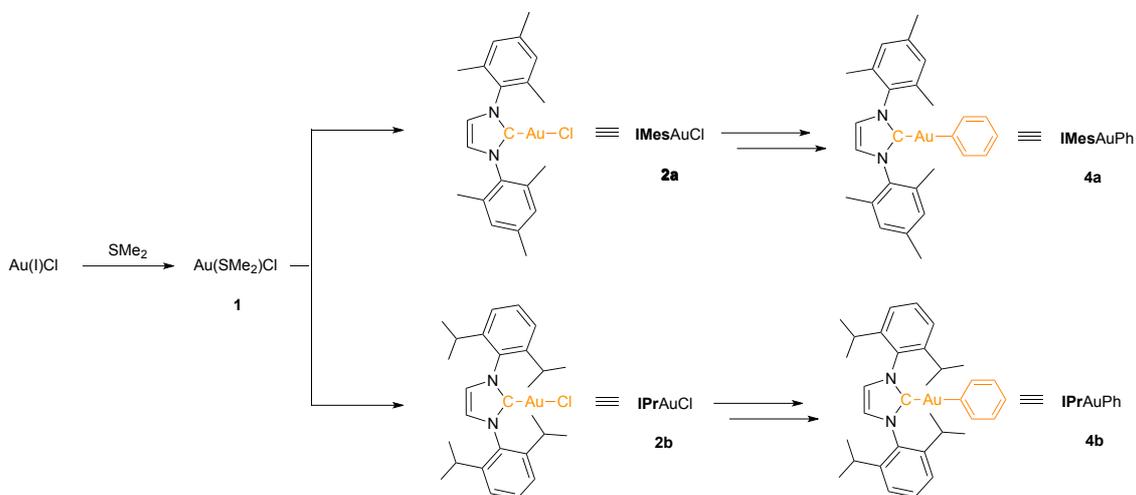


Figure 0. Two proposed mechanisms suggested by Johnson<sup>1</sup> *et al*.

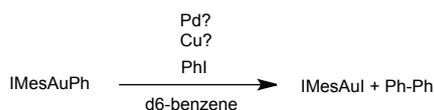
Gold (0) nanoparticles may also possess catalytic activity in cross-coupling reactions shown by Guo<sup>13</sup> *et al*, thus not only the oxidation states (I) and (III). However Guo showed that a large size dependence had an impact on the catalytic effect. Many other gold-mediated homocouplings are discussed in a review by He<sup>14</sup> *et al*, and some recent palladium mediated homocouplings are discussed in a review by Molnar<sup>15</sup> *et al*.

# OBJECTIVE

Novel reactivity of gold(I) complexes such as IMesAuPh (c.f. **4a** in Scheme 1) towards electrophiles such as aryl halide have recently been shown by Johnson<sup>1</sup> and coworkers. However, the kinetics for the new reactivity was to our knowledge unknown, and it would be interesting to investigate it in detail. Furthermore, trace amounts of various catalytically active transition metals such as copper and palladium have previously blinded researchers initially thinking Au(I)-aryls were responsible for the catalytic behavior with aryl halides. Upon further inspection, it was shown that in fact palladium contamination were responsible for catalysis.<sup>12</sup> Unsurprisingly, ICP-MS analysis by Johnson *et al*<sup>1</sup> demonstrated that samples contained non negligible amounts of palladium and copper. Therefore, it would be pivotal to inspect whether addition of or Cu / Pd additives (Scheme 2) would give the same or similar results, and have an impact on product formation of cross-coupling products. It would be additionally interesting to investigate if a slightly modified backbone ligand forming **4b** would render a different reactivity pattern compared to **4a**. Surprisingly, Maier<sup>16</sup> had previously shown an increase in reactivity when forming IPrAuOH from IPrAuCl compared to the IMes counterpart.



**Scheme 1.** A synthetic summary to achieve target compounds IMesAuPh and IPrAuPh.



**Scheme 2.** Reactivity study of the reaction between the Au(I)-aryl IMesAuPh and iodobenzene.



containing, or upon light exposure. Consequently, the grey solid believed to be chloro(dimethylsulfide)gold(I) must have contained large quantities of Au(0). Therefore, the reported high yields gave most likely a false picture and none of the used characterization methods could ascertain a Au(0) free product.

**Table 1.** Entry 1 - 3 giving the experimental data for the formation of chloro(dimethylsulfide)gold(I) following method (i).

Entry	SM (mg)	Equivalents dimetyl sulfide	Rxn time (h)	Temp	Solvent*	Yield (%)	Notes
1	30	Excess (1 mL)	0.5	ambient	Toluene	55	↳ Celite(I)
2	230	Excess (0.9 mL)	0.5	ambient	Toluene	73	↳ Celite(I)
3	728	3 eq (0.8 mL)	0.5	ambient	Toluene	68	↳ Celite(I)

\* Solvents used from the solvent dispenser machine

The problem was readdressed using procedure unpublished protocol from Johnson *et al* (ii), who also reported a grey solid appearance why a new purification method of this first step was required. Despite the grey appearance, this procedure was followed as a yield of 99% was reported. First, the reactions were performed in Strauss flasks with a high vacuum transfer of solvents decreasing the likelihood of water contamination leading to Au(0) formation. Secondly, the crude was filtered through a pad of Celite(R) for Au(0) removal which yielded white crystalline material, this was not reported in the protocol and perhaps had Au(0) formation been overlooked. Unfortunately, upon filtration, low yields ranging from 14-26% were obtained which was unacceptable as the first step in a synthetic route.

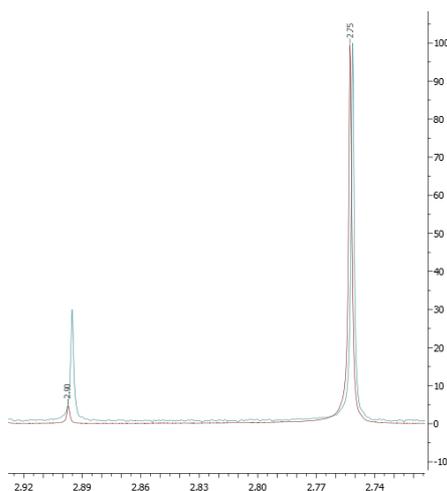
**Table 2.** Experimental data for the formation of chloro(dimethylsulfide)gold(I).

Entry	SM (mg)	Equivalents dimetyl sulfide	Rxn time (h)	Temp	Solvent*	Yield (%)	Notes	Method
1	1004.0***	2 eq (1.6 mL)	3	60	Toluene	16	Filtered	ii
2	632.0	Excess (10 mL)	3	60	N/A	14	Filtered	ii
3	905.2	Excess (10 mL)	3	60	N/A	26	no Celite(R)	ii
4	2043.3	Excess (20 mL)**	24	60	N/A	21	no Celite(R)	ii
5	1040	Excess ( mL)**	2h	0	MeOH	73	no Celite(R)	iii
6	2060	excess (1.1ml)**	10m	0	MeOH	74	no Celite(R)	iii

An approximate 15% reduction of the yield could be concluded between the results where the product had been filtered through Celite(R). Obtaining 16-26% yields in the first step was unacceptable despite reported yields of 95%. In entry 3 and 4 (Table 2), following the reference (ii), a white solid was formed, yet containing yellow impurities.

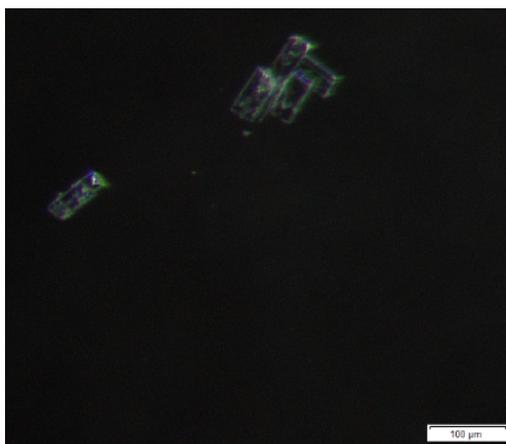
Information from the protocol by Schmidbaur<sup>17</sup> *et al* using ambient reaction temperature, with a recently published procedure from K. Guillois<sup>18</sup> *et al* at 0°C made us believe that the high reaction temperature would likely immediately reduce the Au(I) species to Au(0), leaving only a small part of Au(I) to forming product. The unreacted yellow solids were Au(0) in as much as 75%, this was conclusively determined by dissolution in *aqua regia* upon reprecipitation under basic conditions, no other solvent would dissolve the yellow solids.

A vastly different protocol was reported by K. Gullious<sup>18</sup> *et al* in 2012. This procedure recommend the use of a different precursor, HAuCl<sub>4</sub>, which was dissolved in MeOH followed by dropwise addition of dimethyl sulfide at 0°C, reporting an afforded yield of 80%. The low temperature suggested a key component to avoid any over reduction of Au(III) to Au(0). The reference method was performed using slightly modified conditions. Instead of using the acidic HAuCl<sub>4</sub> salt, KAuCl<sub>4</sub> was used. The reaction time was first followed, however upon the second attempt, the reaction time could be decreased to only 10 minutes, as a white precipitate was immediately forming upon the dropwise addition of reagent. To our satisfaction, no yellow impurities were visually observable. <sup>1</sup>H NMR data still showed the undetermined signal at 2.9 ppm which was now less than 3% of the product peak (2.73 ppm), and a yield of 73% was obtained. By comparing data from the last optimized method (iii) with <sup>1</sup>H NMR data from experimental result using method (ii), it is evident that a reduction of impurity at 2.9 ppm is achieved using method (iii).

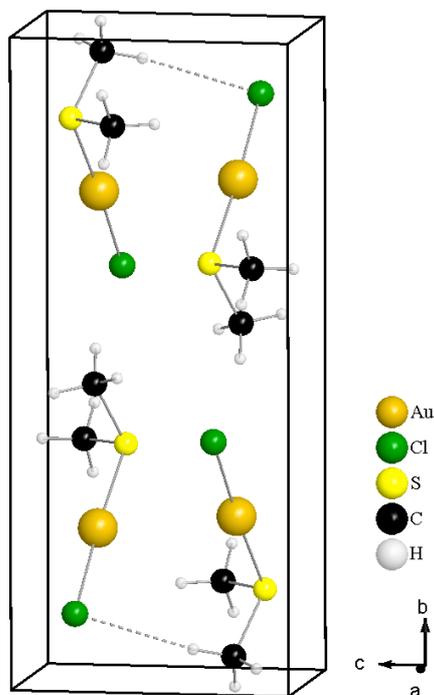


**Figure 1.** NMR spectra of the obtained product following procedure (ii) (blue line) and procedure (iii) (red line). The product peaks at 2.75 ppm are both normalized to 100 in intensity, and both spectra are run using CDCl<sub>3</sub> as internal standard.

A further advantage to method (iii) is that not only is the reaction time shortened, the product was also white crystalline without any need of filtration over Celite(R), as the appearance of the product suggested no Au(0) contents. The procedure was repeated (entry 6, Table 2) while obtaining a 74% yield. A small fraction of the solids were still filtered through a pre-washed Celite(R) pad with benzene and DCM upon subsequent solvent concentration *in vacuo* obtaining crystalline material which was analyzed using a light microscope (Figure 2) showing cuboid shaped crystals which were later measured in the X-ray diffractometer yielding the X-ray structure shown in Figure 3 with all CIF data tabulated in Appendix 9.3. This structure was fully consistent with reported structure by Lautner<sup>19</sup> *et al.*



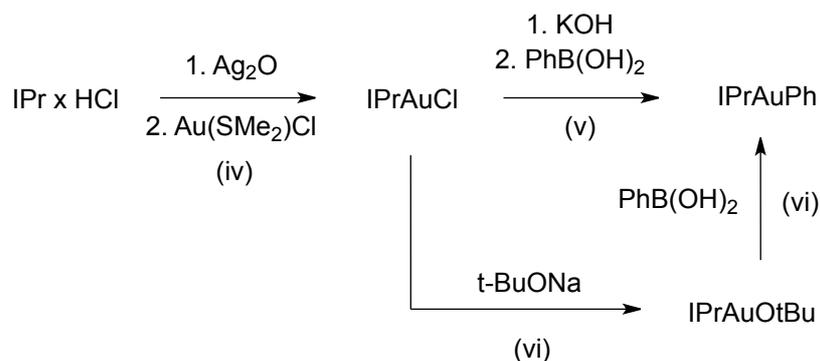
**Figure 2.** Cuboid shaped crystals of chloro(dimethylsulfide)gold(I) shown under magnification using an Olympus SZX16 light microscope.



**Figure 3.** The obtained X-ray structure of chloro(dimethylsulfide)gold(I) showing a cuboidal shaped unit cell.

## 2.2 SYNTHESIS OF IPR GOLD(I) SPECIES

The outlined synthetic routes to the target compound IPrAuPh is shown in Scheme 4. During the synthesis of IPrAuPh, a potential useful purification method was developed, yet the final goal to form IPrAuPh failed. It was not reproducible in a scale large enough to be useful for further reactivity studies to see if the Au(I)aryl complex would be reactive towards aryl halides. The target compounds was only formed in NMR-scale.

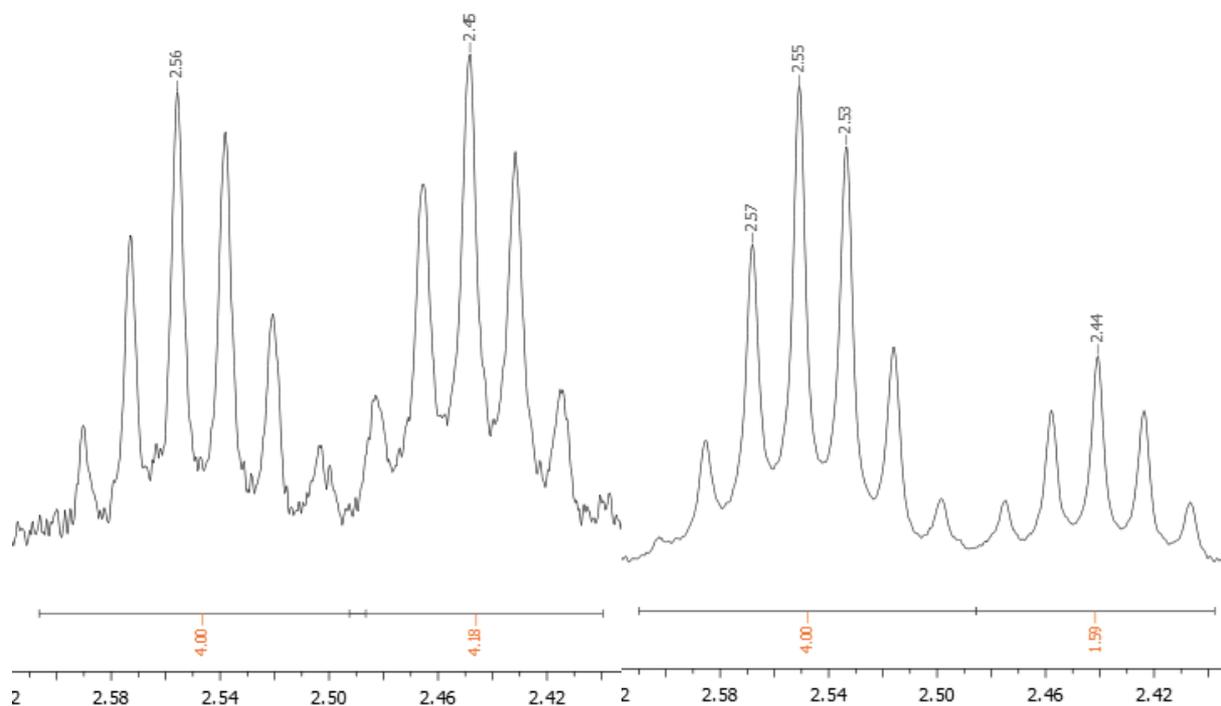


**Scheme 4.** Synthetic route in attempt to form IPrAuPh using protocols reported by Nolan<sup>6</sup> and coworkers from 2010 (iv), by recently (2012) published work by Nolan<sup>7</sup> *et al* (v), and a modified procedure from Johnson<sup>1</sup> *et al* (vi).

Unfortunately, by reacting a large amount of starting material to form IPrAuCl without the knowledge that the majority of the previously made chloro(dimethylsulfide)gold(I) contained up to 75% gold nano particles, product was only formed in a 50% yield, whereas the rest was initially was thought to be IPrHCl due to the shift of signals with the respect to the product peaks. Efforts to purify the product begun by crystallizing the crude in DCM/pentane as reported by Nolan<sup>6</sup>. The large quantity of crude was presumably rendering crystallization unmanageable, even when using a smaller aliquot, crystallization was unsuccessful.

Instead, another reference procedure using unpublished data by Johnson<sup>20</sup> in an effort to purify the crude using column chromatography with 3:2 heptane:ethyl acetate. However, this resulted in complete decomposition of the crude rendering a purple band of Au(0) on the preparative silica plate. This was somewhat surprising since the compound moved on a regular silica 2D TLC without any appearances of decomposition. The gold complexes are known to be sensitive to acid as their nucleophilic Au-X bond may be hydrolyzed. Therefore, a preparative TLC coated with the neutral alumina was also tested. It also showed decomposition and a purple band of Au(0), not immediately but after some time of exposure to the material. Successive crystallizations from DCM/pentane was tried in an effort to purify the crude without any success. One strategy would be to continue synthesis in the next step without further purify product, another would be to find a new method of purification which avoided decomposition of the

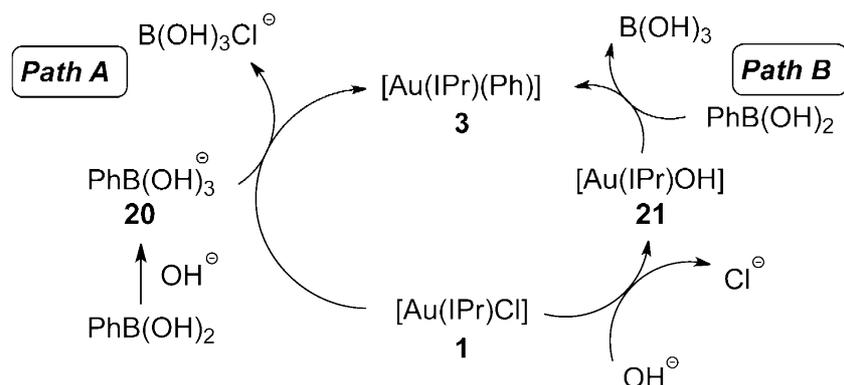
gold(I) complexes. In an attempt to find a new purification protocol, the idea was to take advantage of the large polarity difference between the product and starting material, and an extraction method was developed which results is shown in Figure 4. Nevertheless, it was uncertain whether the gold(I) complex would survive the water solution as these complexes are reported<sup>2</sup> to disproportionate to Au(0) or Au(III) in aqueous media. Sample crude was only fully dissolved in acetone and DCM, and acetone was first tested. Upon addition of water, a turbid suspension resulted. The sample was shaken, evaporated to remove the acetone, upon full precipitation of a solid. The remaining suspension was centrifuged during 20 minutes, and water was then pipetted off. The procedure was repeated three times. When first using normal dram vials, a purple formation occurred suggesting Au(0). The decomposition problem was later eliminated by using amber vials, showing that the light induced decomposition pathway seems more problematic than the disproportionation in aqueous solution for these complexes. As shown in Figure 4, a drastic decrease of starting material was clearly observed after the extraction procedure. Despite efforts of increasing the number of extracting cycles, the distribution remained unchanged. The extraction was also tried using dichloromethane which yielded a poorer purification. It was later discerned that the material was not starting material but the IPrAgCl complex with its similar <sup>1</sup>H NMR.



**Figure 4.** The key identifier proton signal stemming from the isopropyl  $\text{CH}(\text{CH}_3)_2$  group from the IPrAgCl and IPrAuCl (peak at 2.55 ppm) are shown. Crude (two peaks to the left) contained 51% starting material which got reduced after the extraction to only 28% (two peaks to the right) using three extractions in acetone/water as described above. In both figures the peak at 2.56 ppm was normalized to an intensity of 100.

Despite efforts of increasing the number of extracting cycles, changing the solvents, the reduction of impurity would not decrease any further.

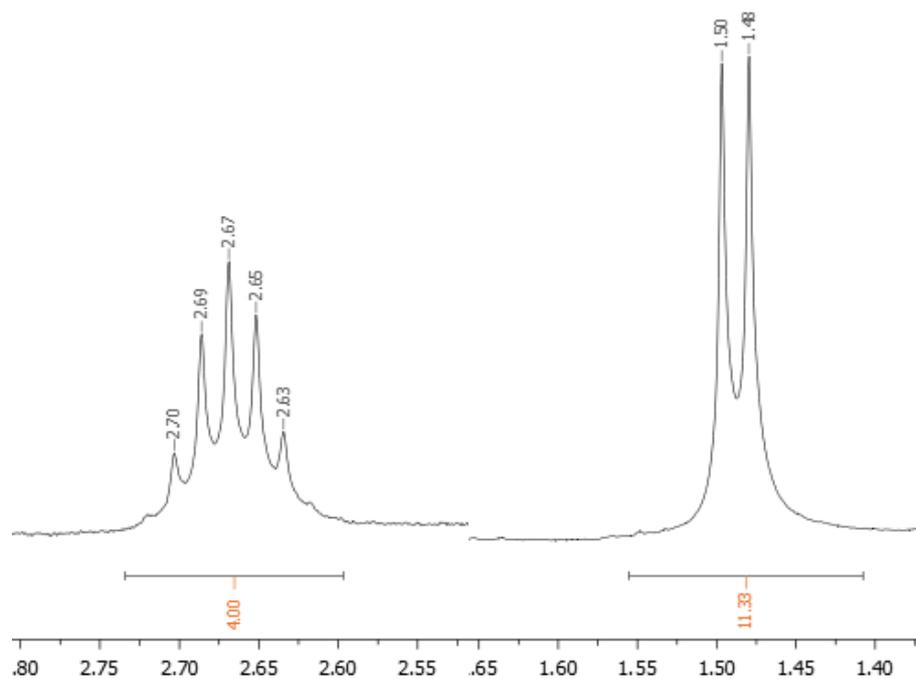
Instead of further purification, it was attempted to form the phenyl complex (IPrAuPh) immediately from the crude containing IPrAuCl using a protocol from recently published data<sup>7</sup> claiming 100% conversion, and using the IPrAuCl specifically. Authors<sup>7</sup> suggested two plausible pathways for the transmetalation between phenyl boronic acid and IPrAuCl which are presented in Figure 5.



**Figure 5.** Two pathways for the conversion of IPrAuCl to IPrAuPh using potassium hydroxide and phenyl boronic acid. Image is adopted from Nolan<sup>7</sup> *et al.*

Upon first attempt, a prolonged reaction time was performed because only starting material and phenyl boronic acid was observable in the crude, even after 24 h. No product was observable. During the second attempt, the reaction time was held exactly (1h). An anticipated color change from yellow to white was observed already within 15 minutes of reaction. The <sup>1</sup>H-NMR spectrum showed product formation but after using the reported workup, only a minimum amount (< 5%) of isolable product was present. The procedure was repeated several times without success isolation of product.

A new strategy was implemented, by first converting the gold chloride to the gold(I) tert-butoxide species which could then be transmetalated into the desired phenyl complex. This procedure would be equivalent to the one reported for the IMes gold species by Johnson<sup>1</sup> *et al* and a protocol from Sadighi<sup>21</sup> *et al* was followed. Due to the impurity of the starting material, a small excess of tert-butoxide was used and the reaction was performed in small scale in a Young tube to be easily monitored, using *d*<sub>6</sub>-benzene at ambient temperature. To our satisfaction, the product had been formed in quantitative yield by <sup>1</sup>H-NMR. Especially important was the 9H peak at 1.39 ppm stemming from the tert-butoxide on the gold complex. The product was not isolated due to the small scale reaction, but was instead prepared for the subsequent addition of phenylboronic acid in an attempt to transmetalate, which successfully showed only product formation and a peak of expected isopropyl alcohol at 1.04 ppm and 0.64 ppm in *d*<sub>6</sub>-benzene. Selected characteristic peaks of the product at 2.66 ppm and 1.48 ppm are shown in Figure 6. No IPrAgCl or IPrAuCl were observable.

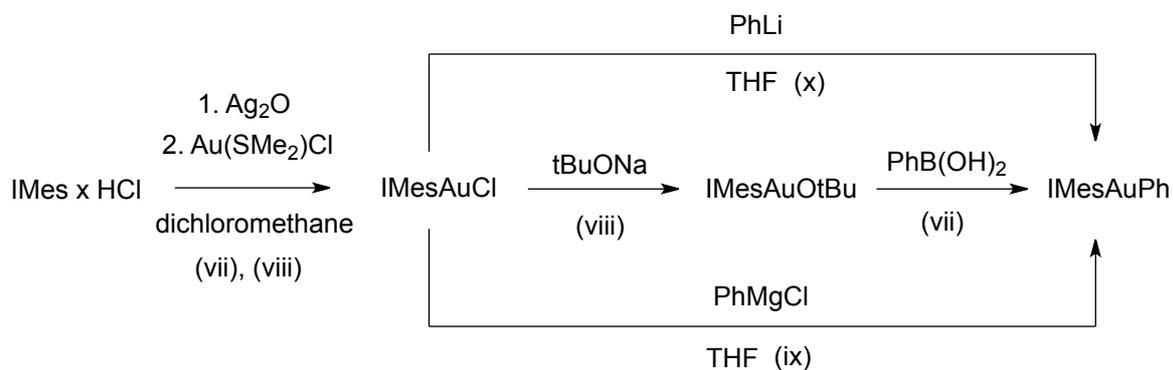


**Figure 6.** Characteristic peaks of IPrAuPh showing a spectrum where 2.67 ppm signal is normalized to the intensity of 100, the integration is with respect to the septuplet at 2.67 ppm.

Unsuccessful attempts to reproduce the above outlined procedure in a larger scale, both by first isolating the tert-butoxide complex and by *in situ* forming the tert-butoxide complex.

When later working with the IMesAuX species, it was discovered that an IMesAgCl complex could form. The earlier believed IPrHCl in the crude of IPrAuCl was in fact IPrAgCl which could also explain why the extraction technique would not work optimal since the polarity difference between IPrAuCl and IPrAgCl is similar.

## 2.3 SYNTHESIS OF IMES GOLD(I) SPECIES

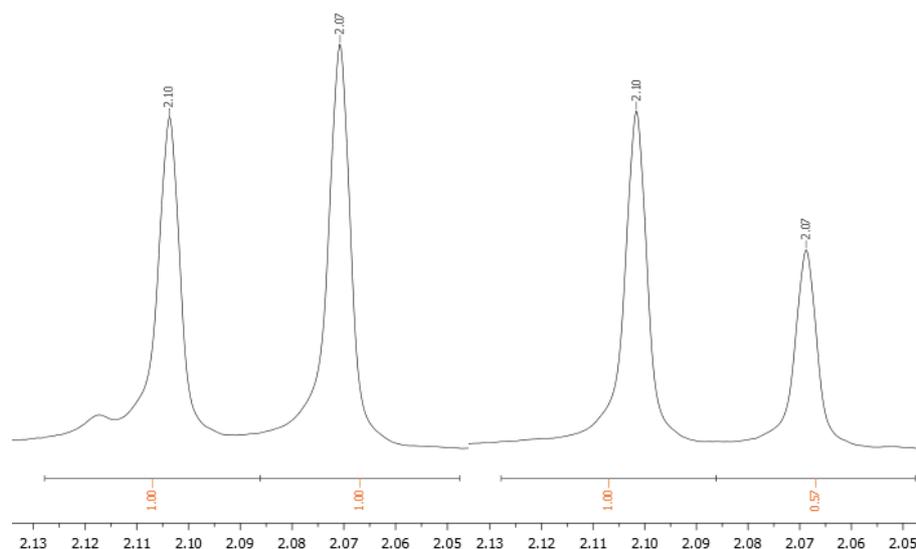


**Scheme 5.** Projected synthetic plan to achieve IMesAuPh using references (vii)<sup>1</sup> and (viii)<sup>1</sup> and (ix) and (x)<sup>22</sup>.

It was important to form the IMesAuPh with a specific procedure avoiding phenyl lithium as reagent, as it is reported that it is produced from PhBr. Therefore it could potentially contain residual phenyl halide causing problem in later kinetical studies.

Previous attempts<sup>1</sup> using the route involving the gold(I) tertbutoxide species was reported in high yields (92%) and the formation of IMesAuPh in 44%. This would therefore be the natural starting point in the synthesis of IMesAuPh.

IMesAuCl was first made using procedure reported by Nolan<sup>6</sup> *et al* suggesting 4h reaction time in DCM with *in situ* formation of IMesAgCl, and to then add the gold(I) species at ambient temperature reaction during 3h but which unfortunately only yielded 6% (isolable) at first attempts, despite full conversion in the <sup>1</sup>H-NMR. Therefore an updated protocol of Nolans work by Johnson<sup>1</sup> *et al* was followed. It was thought that the Ag<sub>2</sub>O may have had an impact on the poor yield as the source was old. Additionally, another references used a higher mole ratio of Ag<sub>2</sub>O without any reported problems. As it was later discovered, the chloro(dimethylsulfide)gold(I) from the first batches contained up to 75% Au(0) nano particles, this was most likely the major contributor to the low yield. Therefore, based on the NMR-ratio of IMesAgCl and IMesAuCl, an additional amount of chloro(dimethylsulfide)gold(I) was added to see if this could decrease the silvercomplex peaks and increased the product peaks (cf. Figure 7) Unfortunately, additional chloro(dimethylsulfide)gold(I) and prolonged stirring gave no further change in relative peak ratio between intermediate and product but only an initial change as shown in Figure 7.



**Figure 7.** Formation of IMesAuCl showing both IMesAuCl together with IMesAgCl before additional chloro(dimethylsulfide)gold(I) was added (left two peaks), and after addition (right two peaks).

Since data showed that further addition of chloro(dimethylsulfide)gold(I) to remaining IMesAgCl did not yield the product in a better ratio, an increased stoichiometric amount from the beginning was used in entry 4-5 (Table 3). This led to only small remains of chloro(dimethylsulfide)gold(I), which in the subsequent reaction to form the tert-butoxide complex seemed to have little effect. From entries 4-8, a better and more pure chloro(dimethylsulfide)gold(I) was used, so only an equimolar amount of it were required. Furthermore, from entry 1-4 solvent from the dispenser system was used which may have explained the low yields as this was unsatisfactory quality. From entry 5-8, distilled dichloromethane was used which was transferred via the high vacuum line. Another factor which could have increased the yields was that a higher mole ratio of  $\text{Ag}_2\text{O}$  was used in entry 4-8. What could have lowered the yield in entry 6 and completely abrupt the reaction in entry 8 was that the magnetic stirring plate caused heat by stirring which presumably decomposed any product.

**Table 3.** In the synthesis of IMesAuCl using two different references and varying the conditions of reagent. \*\* Reaction mixture was involuntarily heated by the magnetic plate.

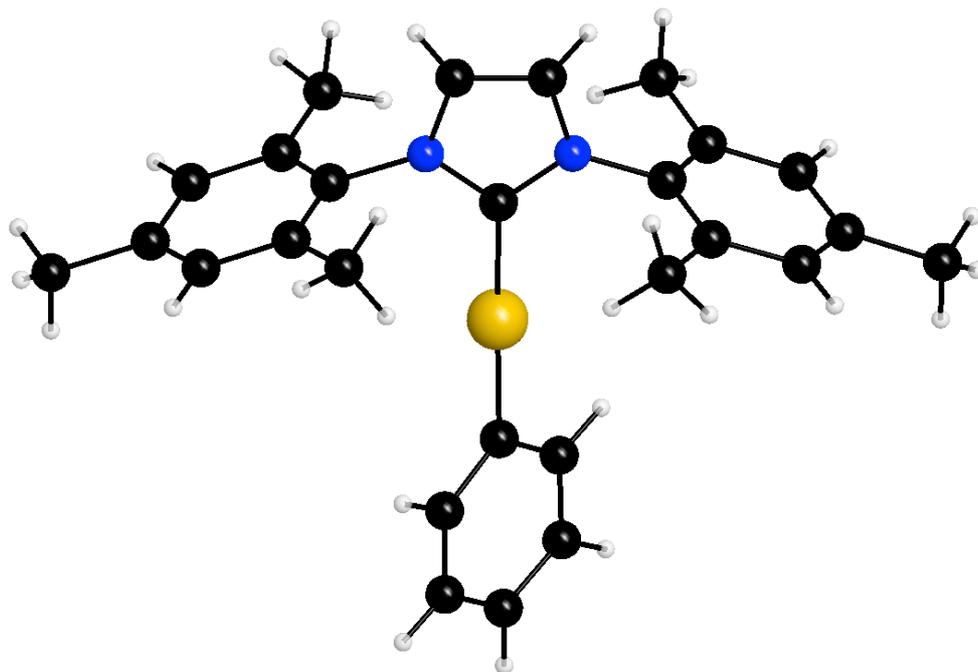
#	Amount SM (mg)	Ag <sub>2</sub> O (mg / eq)	AuS(Me) <sub>2</sub> Cl	Rxn time (h)	Temp	Solvent*	Yield (%)
1	125.5	61.1 / 0.62	100.0 / 0.83	3 days / 2 days	ambient	DCM	6
2	245.0	100.3 / 0.54	201.0 / 0.85	3.5h / 13h	ambient	DCM	61
3	70.4	48.4 / 0.91	58.2 / 0.85	2h / 16	ambient	DCM	N/A
4	70.1	47.0 / 0.88	72.7 / 1.08	2h / 16	ambient	DCM	88 %
5	111.2	74.1 / 0.88	111.2 / 1.04	2h 18 h	ambient	DCM (vacuum line)	100 %
6	99.3	102.5 / 1.36	95.8 / 1.00	2h /14 h	ambient	DCM (vacuum line)	92 %
7	170.79	114.02 / 0.88	164.7 / 1.00	2h / 20h	ambient	DCM (vacuum line)	55 %
8	400.5	198.3 / 0.65	385.9 / 1.00	2h / 10 h	ambient	DCM (vacuum line)	N/A

The second consecutive step (viii) involving the formation of the tert butoxide gold(I) species gave an approximate 50% yield in two reactions and a non isolable yield in one reaction (entry 1, Table 4). The reason for the rather low yield was unclear as in all the entries except 3, a dark purple solution was formed which suggested that Au(0) was formed. It was learned that a rather large pad of Celite(R) had to be used to purify the product and it was necessary to prewash the pad with benzene and avoid dichloromethane as a solvent.

**Table 4.** Synthetic conversion to form IMesAu<sup>t</sup>OBu from IMesAuCl, a: determined by NMR, b: isolable yields

#	SM (mg)	t-BuO (mg / eq)	Rxn time	Temp	Solvent	Yield (%)
1	5.1	1.1* / 1.03	2h	ambient	d6-benzene	100% a)
2	73.6	17.0 / 1.29	3h	ambient	benzene (vacuum line)	44% b)
3	165.5	42 / 1.42	2h	ambient	benzene (vacuum line)	48% b)
4	33	8.2 / 1.38	2h	ambient	benzene (vacuum line)	N/A

Several attempts were made to synthesize the IMesAuPh using phenyl boronic acid which failed. In none of the trials could any product be isolated even though the starting material was clean and the reference procedure was followed from the protocol<sup>1</sup>. Therefore, final attempts to form the product was done by avoiding formation of the tertbutoxide gold complex and by avoiding usage of phenyl lithium. A modified procedure from Nolan<sup>22</sup> *et al* (ix) 2005 was used to successfully convert IMesAuCl directly in one step to the desired compound in a 25% yield. The modified procedure involved the use of PhMgCl instead of PhMgBr. Additionally, due to anticipated decrease in reactivity, reaction was prolonged from 2h to 12h. Reported purification strategy involved flash chromatography using alumina in THF/hexane, with extreme care to increase the flow rate to decrease the amount of decomposition. Upon purification, crystals were growing in three of the fractions, which was collected and measured in the X-ray diffractometer. Crystallographic data showed the target compounds with two molecules in one unit cell (Figure 8). The remaining CIF data file is appended in the Appendix.

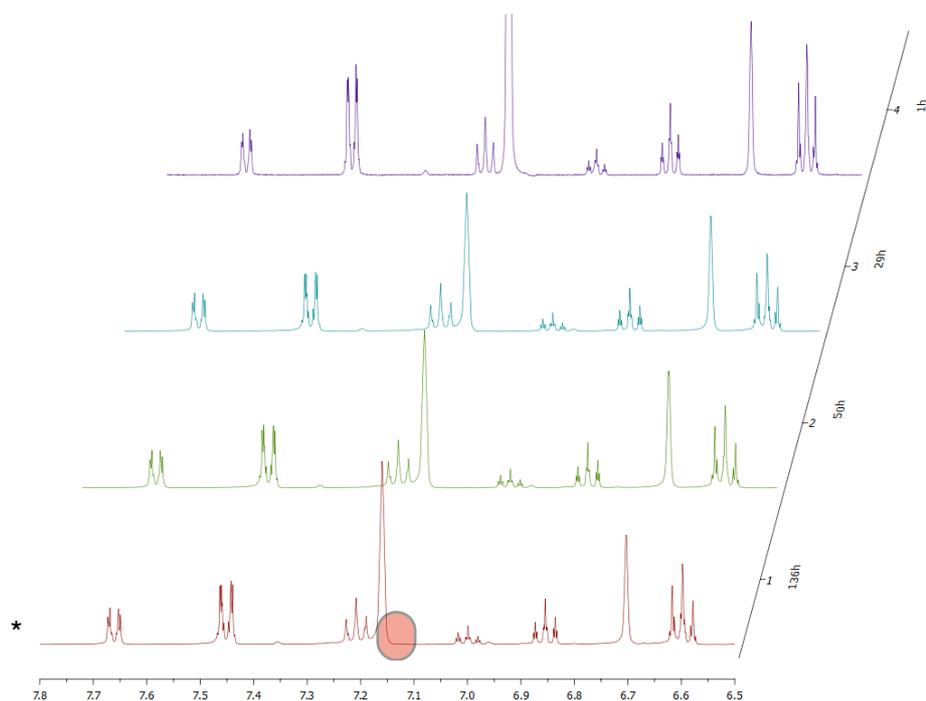


**Figure 8.** Crystallographic structure of IMesAuPh.

## 2.4 REACTIVITY EXPERIMENTS USING IMESAUPH

The mechanism of gold-mediated coupling reactions have been debated as it have been shown that small amounts of palladium sources can catalyze reactions originally thought being gold catalyzed.<sup>12</sup> Recent work by M. Johnson<sup>1</sup> *et al* showed a complete new reactivity towards aryl halides, where Au(I)-aryl were suggested as a n intermediate in the cross coupling formation forming biphenyl.

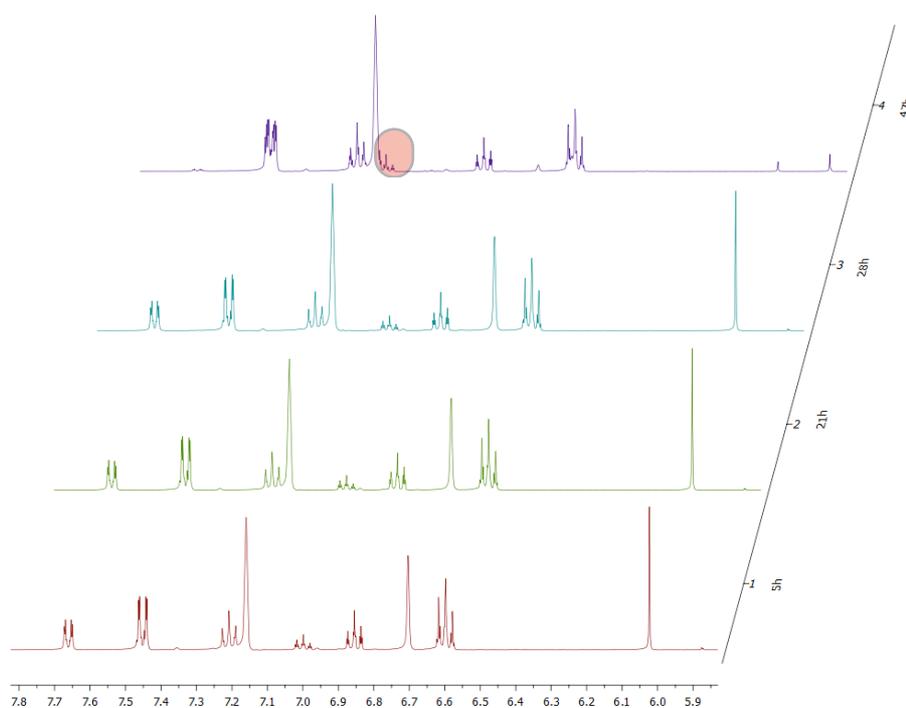
Thus, to further investigate this new reactivity, and to obtain a more thorough and fundamental understanding of the potential underlying mechanism, the specific reaction of IMesAuPh with PhI at 110°C in benzene was explored. Due to limitations set by the probe in the NMR, the reaction temperature could only reach 90°C. Surprisingly, from array experiments during 17 h, there was no observable biphenyl cross-coupled product formed. As seen in the stacked spectra (Figure 9), no change occurred even after a prolonged reaction time of 136 h at 90°C. Any anticipated biphenyl formation would show three peaks of which two is covered under iodobenzene (6.86 ppm, 7.46 ppm), and one at 7.11 ppm, somewhat upfield to the C<sub>6</sub>H<sub>6</sub>.



**Figure 9.** Reaction of IMesAuPh with phenyl iodide in d<sub>6</sub>-benzene using an internal standard of cyclooctane at 90°C. IS are used to normalize all spectra. The peaks where biphenyl should be visible is highlighted with a red box. NMR are recorded at 400 MHz (\*500 MHz).

By further examine if the IMesAuPh would decompose over time, the internal standard (IS) was integrated and set to 16.0 protons and compared to the AuPh peak at 7.67 ppm in all runs. Only a 5% decrease in intensity was observed from the 29 h to 136 h reaction in the 90°C experiment. After the first 17 h of reaction, there was no observable color change in the transparent solution. Interestingly, after 136 h, a fade pink color was observed suggesting Au(0) formation by decomposition of the Au(I) NHC complex.

The same sample was further investigated at an elevated temperature (110°C) to investigate whether the reaction temperature could cause a change even though it had been compensated by the prolonged reaction time. No product formation was observed during the first 28 hours, but after 47 hours the IMesAuPh had been reduced in concentration and a limited amount of biphenyl was observe by the peak at 7.11 (Figure 10). An additional characterization tool supporting the biphenyl formation was the complexity of peak at 7.48 ppm. Additionally, from the 5 h scan to the 47 h scan at 110°C, the IMesAuPh was reduced in concentration by 83% by comparison to the IS as described above. However, from scan 5 h to 21 h scan, the complex was only reduced by 2%. The long reaction time would suggest Au(0) nanoparticle formation to be supported by an induction time suggested by Lambert *et al.*



**Figure 10.** The reaction of IMesAuPh with phenyl iodide in  $d_6$ -benzene using an internal standard of cyclooctane at 110°C using a 400 MHz NMR. No observable

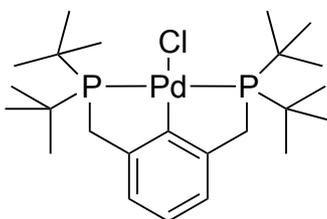
amount of biphenyl was observed during the first 28 h. After 47 h, short biphenyl peak is observable at 7.11 ppm (red box), while the Au(I) NHC was consumed.

The spectra in Figure 10 were normalized to 100 in intensity with respect to the internal standard. The reaction showed high amounts of presumably Au(0) nanoparticles as a pink/purple layer had formed on the walls of the J. Young tube after 47 h at 110°C, but not after 137 h at 90°C. Then, only a minimum pink color was observed from an angle parallel with the tube (Figure 11). This in combination with the late formation of biphenyl suggest that the cross-coupling may be catalyzed by Au(0) nanoparticles.



**Figure 11.** The NMR-tube from the same experiment containing IMesAuPh, internal standard, and phenyl iodide after 137 h at 90°C (left) and after the additional 47 h at 110°C (right).

Authors<sup>1</sup> had previously showed by ICP-MS that samples contained significant amounts of Pd and Cu. Therefore, it further experiments were repeated using the same protocol but by in parallel studying three reactions in separate sample tubes, all containing IMesAuPh, PhI, and IS. To one of the tubes were added a Pd source (Figure 12) in a stoichiometric amount, and to the third was added CuI as the copper source also in a stoichiometric amount.

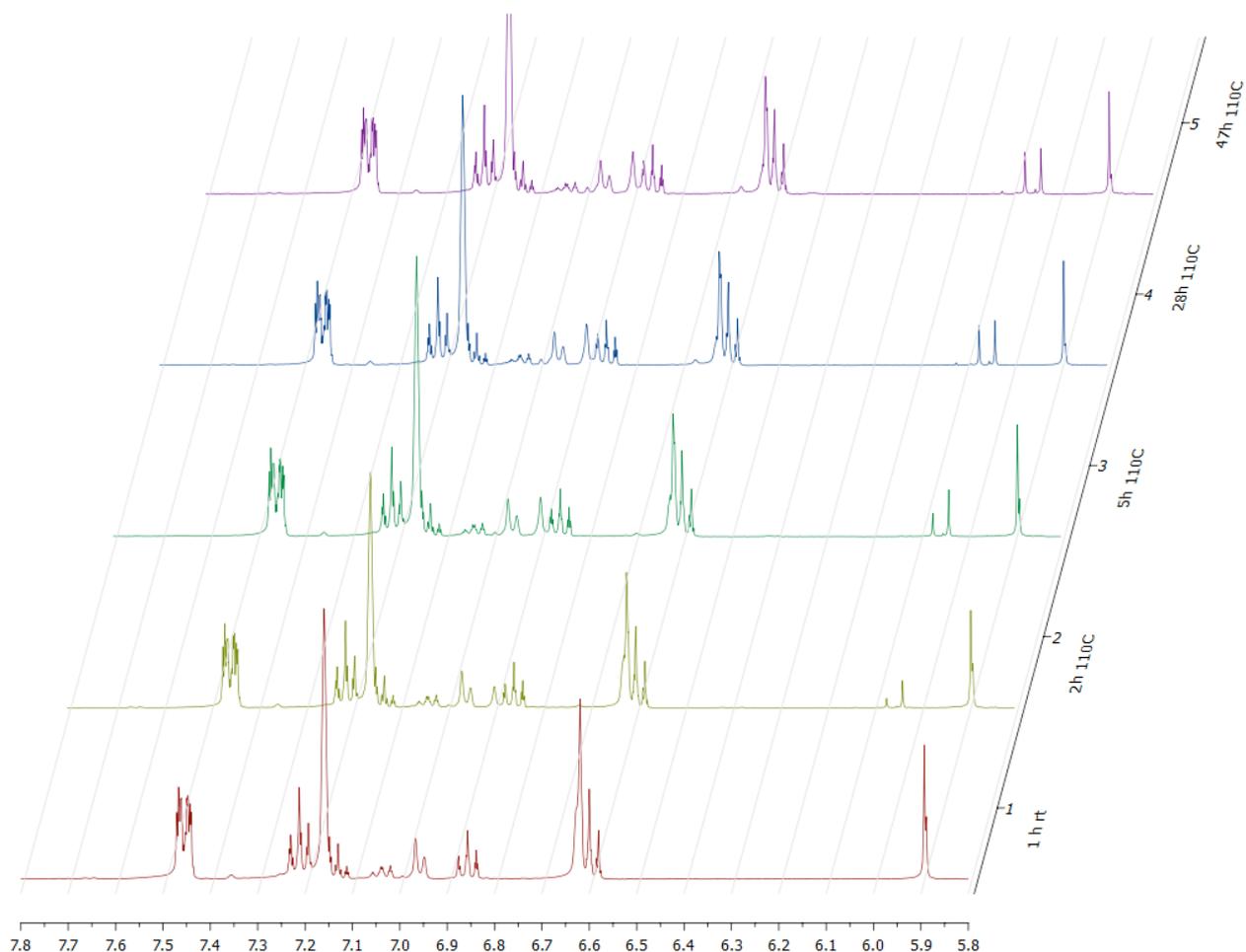


**Figure 12.** The structure of the palladium pincer complex which was used the palladium source.

The first experiments without additives showed an 8% decrease of IMesAuPh relative to the IS after 21 h, and 16% decrease after 47 h. Biphenyl formation was

not observable until the 47 h measurement. This reproducibility provided extra support to the initial data suggesting that Au(0) probably catalyzed the reaction.

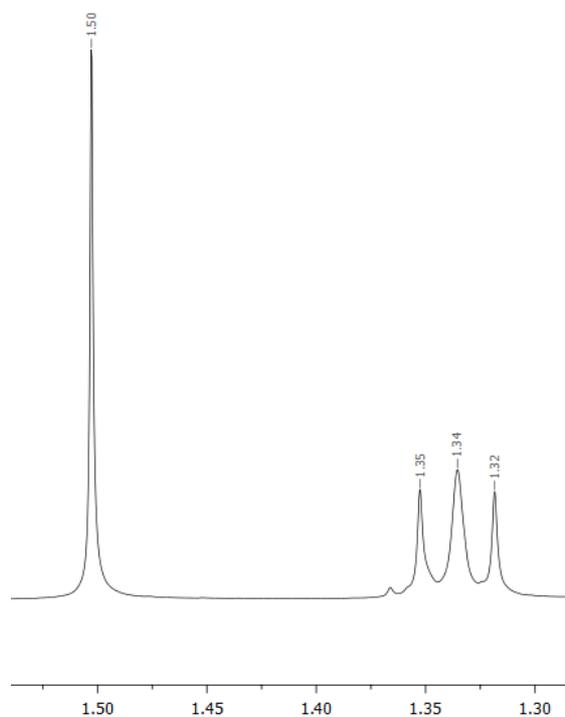
Upon adding the pincer complex to the sample, a yellow suspension with a black precipitate formed immediately. NMR was not measured until 1 h at room temperature (Figure 13).



**Figure 13.** Featuring the key region 7.8-5.8 ppm of the reaction of IMesAuPh with phenyl iodide in  $d_6$ -benzene using an internal standard of cyclooctane at 110°C, monitoring using a 400 MHz NMR. Biphenyl was observed immediately at room temperature, while the Au(I) NHC was converted into IMesAuI. All spectra were normalized to 100 in intensity using the internal standard.

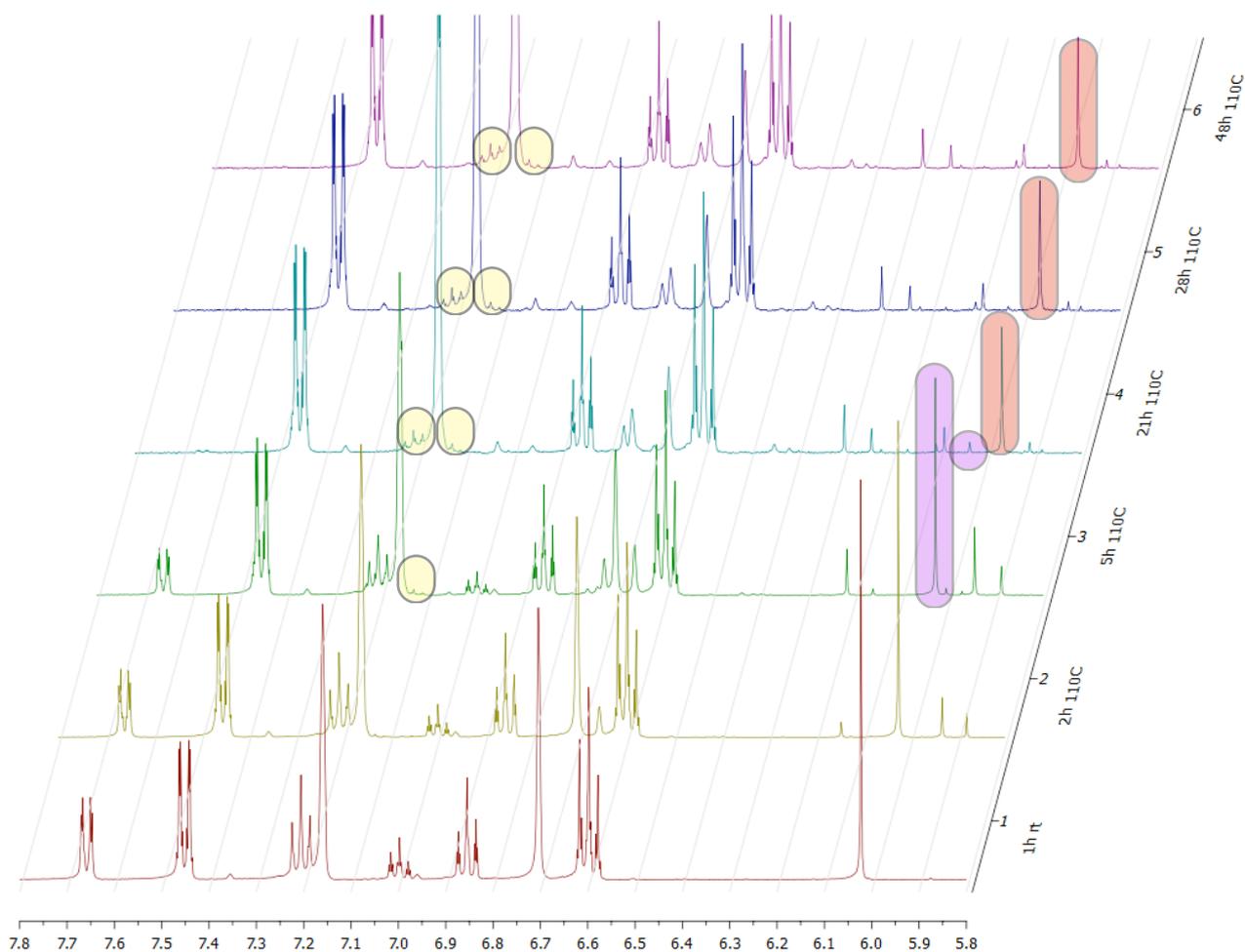
The result showed that IMesAuPh had been fully converted into IMesAuI given by the peak at 5.9 ppm and the peak at 6.62 ppm. An unidentified byproduct at 6.07 and 6.04 ppm had also formed. Interestingly, biphenyl had formed and it was evident that stoichiometric amount of a palladium source was either alone responsible for the formation of biphenyl, or dual catalysis where palladium in concert with gold catalyzed the reaction. The pincer complex did not show evidence of decomposition by comparing its relative intensity from the IS (Figure

14) measurement at 1 h to 47 h. One could otherwise believe that it had decomposed to Pd(0) which in turn would catalyze the reaction. This would still be plausible if any reactivity of the pincer complex had been ongoing before the first NMR measurement.



**Figure 14.** The triplet at 1.34 ppm arising from the tert-butyl groups on the pincer complex in the sample from the reaction with IMesAuPh and PhI.

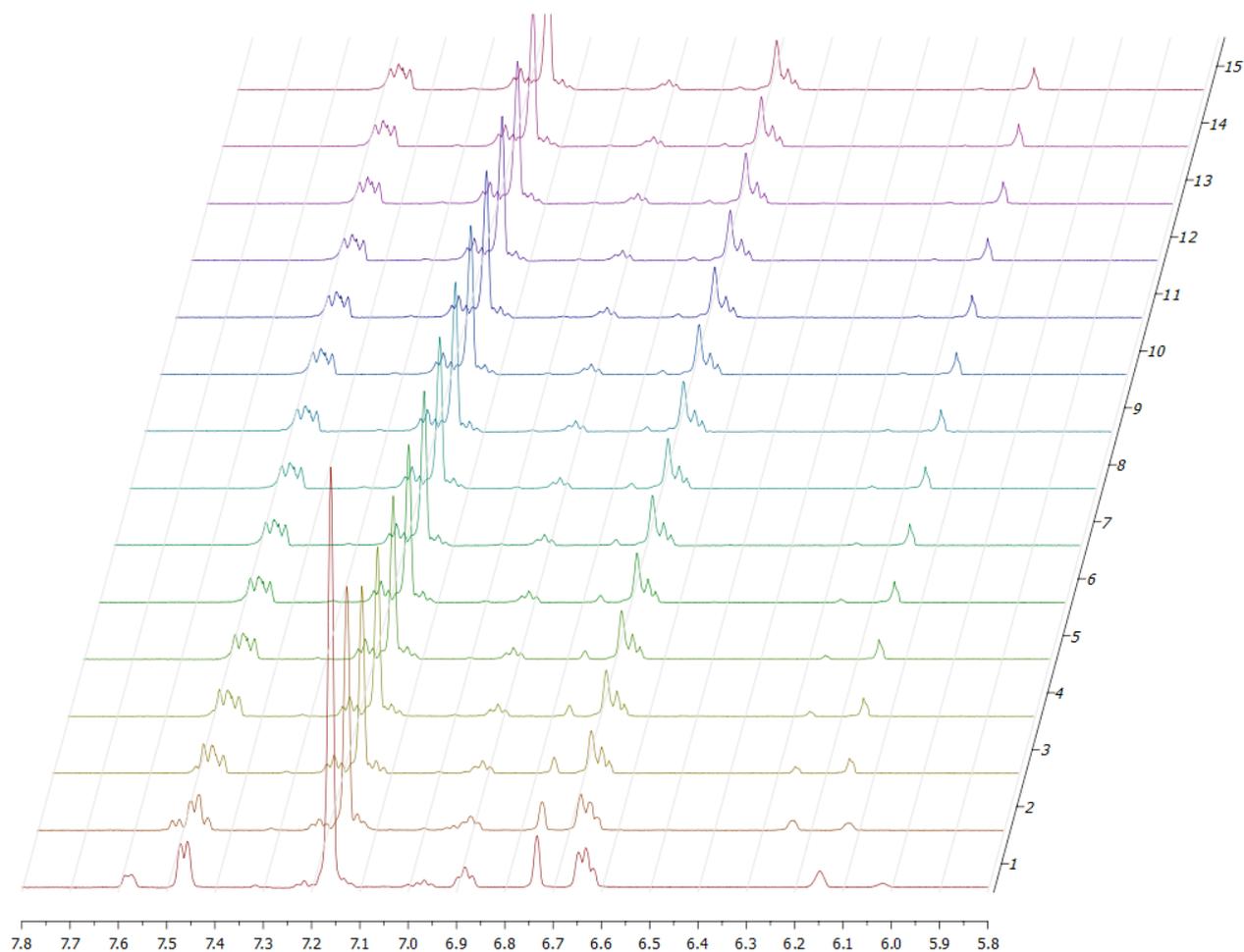
The second aspect of investigation was the if copper could have an impact on catalysis. Data showed a progressively decrease of IMesAuPh (purple highlight, Figure 15) which was depleted after 21 h. The peak at 6.03 ppm inherent to IMesAuPh changed at 21 h to 5.95 ppm belonging to IMesAuI, which could also be observed by the peak at 6.62 ppm. Additionally, biphenyl was formed already after 5 h shown by the weak peaks at 7.13 and 7.11 which were intensified over time. Also, the biphenyl formation was further supported by the full removal of IMesAuPh at 7.67 peak, while still maintaining the multiplet at 7.21 which only got reduced in intensity, as the biphenyl should have a multiplet at 7.21. Clearly, Cu(I) could catalyze the system but additional species or intermediates were also formed which were not formed in the copper free system (control experiment). Therefore it seems unlikely that copper contaminants affected catalysis.



**Figure 15.** Featuring the key region 7.8-5.8 ppm for the reaction of IMesAuPh with phenyl iodide in  $d_6$ -benzene using an internal standard of cyclooctane at  $110^\circ\text{C}$  and CuI, monitoring using a 400 MHz NMR. Biphenyl was observed at 5 h at  $110^\circ\text{C}$ , while the Au(I) NHC was completely converted into IMesAuI. All spectra were normalized to 100 in intensity using the internal standard.

The last experiment investigated whether a catalytic amount (1 mol%) of Pd in the form of the pincer complex could give a similar effect to the one observed using a stoichiometric amount.

Already in the first minutes at 90°C, the gold complex had been converted to IMesAuI and biphenyl was formed (Figure 16). After first studying the reaction at room temperature, no observable changes were observable after 30 minutes. Thus, even a catalytic amount of palladium could be responsible for formation of biphenyl. After the stacked spectra were run, a NMR at ambient temperature was run which more clearly confirmed cross coupling product and that IMesAuPh had been fully converted into IMesAuI.



**Figure 16.** Featuring the key region 7.8-5.8 ppm of the reaction of IMesAuPh with phenyl iodide in  $d_6$ -benzene using an internal standard of cyclooctane at 90°C and PCP-PdCl in a catalytic amount, monitoring using a 400 MHz NMR. Biphenyl was observed immediately at 90°C, while the Au(I) NHC was converted into IMesAuI. All spectra were normalized to 100 in intensity using the internal standard. All spectra are run with in a total of 30 minutes, 2 minutes each. The high temperature made the peaks less intense.

Further experiments were run trying to understand whether mercury could impede the reaction when a catalytic palladium amount was added. Similarly, two experiments, one control, and one Hg containing samples were prepared.

To ascertain that the Hg itself had no impact on reactivity, both samples were reacted at 110°C overnight and to one Hg(1) was added in excess. Surprisingly, already after 1 h, black solids and a yellow suspension was observable, and a poor  $^1\text{H}$ -NMR spectrum was recorded. After additional 23 h, the NMR was rerun showing only a  $\text{C}_6\text{H}_6$  peak together with the internal standard. Perhaps had the gold complex reacted with the mercury resulting in decomposition, also leaving the ligand NHC insoluble in benzene.

# EXPERIMENTAL DATA

## 3.0 General remarks

All manipulations was carried out in the absence of light using Strauss flasks covered in aluminum foil, preferably several layers or in amber reaction vessels. All solvents were distilled used from appropriate drying agent (see Chemicals below) under vacuum transfer directly to the reaction vessel. All experiments were carried out under an atmosphere of nitrogen. Stir-bars and J. Young NMR-tubes were washed in freshly prepared *aqua regia* prior to use. NMR experiments were carried out using J. Young NMR tubes.  $^1\text{H}$ -NMR experiments were recorded on a Varian Unity INOVA 500 spectrometer operating at 499.77 MHz ( $^1\text{H}$ ), a Bruker 400 spectrometer operating at 400.13 MHz ( $^1\text{H}$ ). Chemical shifts are given in ppm downfield from TMS using residual solvent peaks ( $^1\text{H}$ -NMR) as internal standards. Multiplicities are abbreviated as follows: (s) singlet, (d) doublet, (t) triplet, (q) quartet, (sept) septuplet, (m) multiplet, (b) broad, (v) virtual. All chemicals were used without further purification: dimethyl sulfide (Sigma Aldrich, 25 mL, >99%), dimethyl sulfide (Acros, 500 mL, >99+%), AuCl (Alfa Aesar, 99.9 % trace metal), AuCl (1g, Acros, 99+% under  $\text{N}_2$ ), KOH (Scharlau pellet, ACS, ISO reagent grade, Fischer Scientific),  $\text{Ag}_2\text{O}$  (250g, Lab BDH chemie, >97%),  $\text{AuCl}_3$  (5g, Sigma Aldrich), CuI (100g, Merck),  $\text{PhB}(\text{OH})_2$  (Alfa Aesar, 99%), sodium tert-butoxide (Acros, 99%). Methanol was distilled and stored over  $\text{Mg}(\text{OMe})_2$ , dichloromethane were distilled and stored over  $\text{CaH}_2$ , toluene benzene were distilled and stored over Na and  $\text{Ph}_2\text{CO}$ .

## 3.1 SYNTHESIS OF CHLORO(DIMETHYLSULFIDE)GOLD(I)

Only the updated protocol from the a modified procedure of Guillois<sup>18</sup> *et al* is used as this showed the highest yield with the highest purity in question.

### **Chloro(dimethylsulfide)gold(I)**

All manipulations were carried out in the absence of light by covering the reaction vessel (Strauss flask) in aluminum foil. An excess of dimethyl sulfide had previously been vacuum transferred to ascertain purity.  $\text{KAuCl}_4$  (2.06 g, 5.45 mmol) had prior to use been dried under high vacuum line during 30 minutes, upon vacuum transfer of distilled MeOH. To the yellow solution of  $\text{KAuCl}_4$  at 0°C under  $\text{N}_2$  (glovebox), was added dropwise the vacuum transferred excess of dimethyl sulfide (1.1 mL, 22.1 mmol) forming an orange suspension. Within 5 minutes of stirring a white precipitate occurred. The white solids were washed under air with cold methanol (4 x 15 mL) by decanting the solution from the Strauss flask leaving the white solids to evaporate *in vacuo*. It is important to avoid addition of warm (room temperature) methanol as the solids may begin to decompose. The white solids were dried under the high vacuum line to afford 1.15 g (3.9 mmol) of product (72%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): 2.73 (s, 6H). Crystallization from benzene and dichloromethane upon subsequent filtration over Celite(R) yielded crystalline material which was analyzed by X-ray crystallography confirming the structure.

## 3.2 IPR-GOLD(I) SPECIES

### **IPrAu-*t*-OBu**

Modified protocol from Sadighi<sup>21</sup> *et al.* In a glovebox, a 0.6 mL d<sub>6</sub>-benzene was added to a Young tube prepared with 10.8 mg (0.020 mmol) of starting material (IPrAuCl). After 10 minutes, potassium *tert*-butoxide (5 mg, 0.044 mmol) was added all at once, the contents was well mixed, and the tube was covered in aluminum foil. After 3h, a white suspension was observed furnishing the product in quantitative yield<sup>1</sup>. <sup>1</sup>H-NMR (d<sub>6</sub>-benzene, 400.13 MHz): δ 7.23 (m, *J* = 7.6 Hz, 6H, para-CH, meta-CH), 7.07 (s, 2H, NCH), 2.60 (sept, *J* = 6.8 Hz, 4H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.44 (d, *J* = 6.8 Hz, 12H, CH(CH<sub>3</sub>)<sub>2</sub>) 1.39 (s, 9H, OC(CH<sub>3</sub>)<sub>3</sub>), 1.05 (d, *J* = 7.2 Hz, 12H, CH(CH<sub>3</sub>)<sub>2</sub>).

### **IPrAuPh**

In a glovebox, the gold(I) *tert*-butoxide complex (10.8 mg, 0.016 mmol) was suspended in a solution of d<sub>6</sub>-benzene (0.6 mL) in a Young tube to which phenyl boronic acid (2.2 mg, 0.018 mmol) was added. Within one hour, the product had formed in a quantitative yield<sup>1a,23</sup>. <sup>1</sup>H-NMR (d<sub>6</sub>-benzene, 400.13 MHz): δ 7.53 (dd, *J* = 8.0, 1.2 Hz, 2H, C<sub>6</sub>H<sub>5</sub>), 7.16 - 7.23 (m, 4H, IPr para-CH + C<sub>6</sub>H<sub>5</sub>), 7.09 (d, *J* = 8.0 Hz, 4H, IPr meta-CH), 6.99 (tt, *J* = 7.6, 1.2 Hz, 1H, para-C<sub>6</sub>H<sub>5</sub>), 6.31 (s, 2H, NCH), 2.67 (sept, *J* = 6.8 Hz, 4H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.49 (d, *J* = 6.8 Hz, 12H, CH(CH<sub>3</sub>)<sub>2</sub>) 1.10 (d, *J* = 6.8 Hz, 12H, CH(CH<sub>3</sub>)<sub>2</sub>).

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<sup>1a</sup> Determined by <sup>1</sup>H-NMR

### 3.3 IMES GOLD (I) SPECIES

#### **IMesAuCl**

Ag<sub>2</sub>O (74.1 mg, 0.31 mmol) and IMesHCl (111.2 mg, 0.37 mmol) was added to a Strauss flask inside glovebox. Dichloromethane (10 mL) was then vacuum transferred to the vessel and it was stirred for 3 hours in the dark. Another Strauss flask was loaded with chloro(dimethylsulfide)gold(I) (112.9 mg, 0.38 mmol) and the formed in situ formed silver complex was filtered into the Strauss flask with the gold(I) complex to stir overnight. The resulting white suspension was filtered through a pad of Celite(R) and evaporated *in vacuo* to afford 199 mg (0.37 mmol) (100%). <sup>1</sup>H-NMR (d<sub>1</sub>-chloroform, 400.13 MHz): δ 7.09 (s, 2H, NCH), 6.99 (s, 4H, CH), 2.35 (s, 6H, para-CH<sub>3</sub>), 2.10 (s, 12H, ortho-CH<sub>3</sub>).

#### **IMesAu-t-OBu**

IMesAuCl (73.6 mg, 0.14 mmol) was drying during 30 min on the high vacuum line. To the Strauss flask, sodium tertbutoxide (17.0 mg, 0.18 mmol) was added and benzene (10 mL) was transferred using the high vacuum line. The mixture was stirring during 1 hour in the dark. The suspension was filtered through a 4 cm Celite(R) pad into a new Strauss flask, after it was dried on the high vacuum line to furnishing the product in 44% yield 35 mg (0.06 mmol). <sup>1</sup>H-NMR (d<sub>6</sub>-benzene, 400.13 MHz): δ 6.70 (s, 4H, ArCH), 5.93 (s, 2H, NCH), 2.10 (s, 6H, para-CH<sub>3</sub>), 1.95 (s, 12H, ortho-CH<sub>3</sub>), 1.45 (s, 9H, OC(CH<sub>3</sub>)<sub>3</sub>).

#### **IMesAuPh**

A Strauss flask equipped with IMesAuCl (240.8 mg, 0.45 mmol) and a stirbar was dried on the high vacuum line for 30 min upon transfer of tetrahydrofuran (10 mL). The solution was cooled to 0C in the glovebox upon dropwise addition of PhMgCl (0.9 mL, 1.78 mmol), a slow color change occurred. The solution was put in the freezer (-29C) overnight. It was then opened to air, and purified on flash chromatography using hexane: THF, 9:1 to afford 65.9 mg (0.11 mmol) (25%) of product. <sup>1</sup>H-NMR (d<sub>6</sub>-benzene, 400.13 MHz): δ 7.66 (dd, *J* = 7.6, 1.2 Hz, 2H, C<sub>6</sub>H<sub>5</sub>), 7.21 (m, 2H, C<sub>6</sub>H<sub>5</sub>), 7.00 (tt, *J* = 7.2, 1.2 Hz, C<sub>6</sub>H<sub>5</sub>), 6.70 (s, 4H, meta-CH), 6.02 (s, 2H, NCH), 2.06 (s, 6H, para-CH<sub>3</sub>), 2.05 (s, 12H, ortho-CH<sub>3</sub>).

## 3.4 REACTIVITY EXPERIMENTS

All preparations of the kinetic experiments were performed in glove box environment ( $N_2$ ) using micropipettes which had been pumped in wrapped in aluminum foil. All stock solutions were stored in  $-29^\circ\text{C}$  freezer in glove box environment in amber drams. A stock solution of iodobenzene was prepared from 25  $\mu\text{L}$  PhI in 1000  $\mu\text{L}$   $d_6$ -benzene. The internal standard (cyclooctane) was prepared a stock solution of 25  $\mu\text{L}$  cyclooctane in 1000  $\mu\text{L}$   $d_6$ -benzene. The starting material was prepared by taking 65.9 mg dissolving of IMesAuPh (crystals solid only) in 4000  $\mu\text{L}$   $d_6$ -benzene.

All preparations of experiments were done in parallel to avoid any discrepancy, and by first adding 200  $\mu\text{L}$  of  $d_6$ -benzene to a dram vial, to which PhI (24.2  $\mu\text{L}$ ) from the stock solution was added, internal standard (26.4  $\mu\text{L}$ ), starting material (182  $\mu\text{L}$ ), and then any additives such as CuI, PCP-Pd-Cl complex. The vial was well mixed and the contents was added to the J. Young tubes. The drams was then rinsed with additional 200  $\mu\text{L}$   $d_6$ -benzene which was also transferred to the NMR tubes. The mercury droplet experiment was prepared as above samples but including the addition of Hg(l) (67 mg).

Samples were measured on the NMR all consecutively, and when all NMR were recorded, the samples were immediately reinserted onto the oil bath at  $110^\circ\text{C}$ , and covered in aluminum foil. Time was only accounted for when the samples was in the oil bath. The samples were in the same oil bath.

# CONCLUSIONS

Several compounds were synthesized and improved synthetic transformations were accomplished. Updated crystal structures of AuSMe<sub>2</sub>Cl and of IMesAuPh were achieved.

Our data indicated that Au(0) nano-particles might be responsible for catalysis as the reaction at a slightly lower temperature yielded no biphenyl formation, even at extensively prolonged reaction time. Whether palladium sources could affect the reaction using both a stoichiometric and a catalytic amounts, showed that IMesAuI formed and that the NHC-Au(I)-Ph immediately reacted and thus acted as a mechanistic intermediates in the CC coupling.

In the case of copper addition, formation of IMesAuI also formed initially but was eventually consumed. Thus, other compounds formed suggesting that copper contaminant most likely did was not involved in the CC coupling as these species was not observed in the control experiments. This data does thus not exclude the previously believed suggestions where NHC-Au(I)-Ph complexes would serve as a mechanistic intermediate, but rather supports the idea of that the Au(I)-Ph is not the species responsible for the catalytic effect, it most likely catalysis with either palladium, or as our data most strongly suggest: Au(0) nanoparticle catalysis alone.

Further control experiments are necessary using even smaller amounts of Cu and Pd as reported values by ICP-MS to be found in a typical sample showed 303 ppm of Cu and 616 ppm of Pd. To conclusively confirm that catalysis is Au(0) based, further investigation is required including experiments which *in situ* decomposes the gold(I) complex at a higher rate, forming Au(0).

# FUTURE PROSPECTIVES

It would be of interest to again use the modified Nolan procedure which successfully formed IMesAuPh in one step, and to further study the reactivity towards the electrophiles used by Johnson<sup>1</sup> *et al*, and enlarge the scope. Perhaps could any comparative effect having the IPr ligand also be observed using the same protocol.

Additionally, more control experiments involving the addition of Pd(0) sources with defined properties, or PCP complexes in the same amount as the published reference to to each sample, to investigate if the reactivity could be reproduced.

It would be profoundly important to add an external and well defined size type of Au(0) nano particles to investigate if the formation of biphenyl would occur on a faster basis, or an agent which would decompose the Au(I) species *in situ* at a faster rate.

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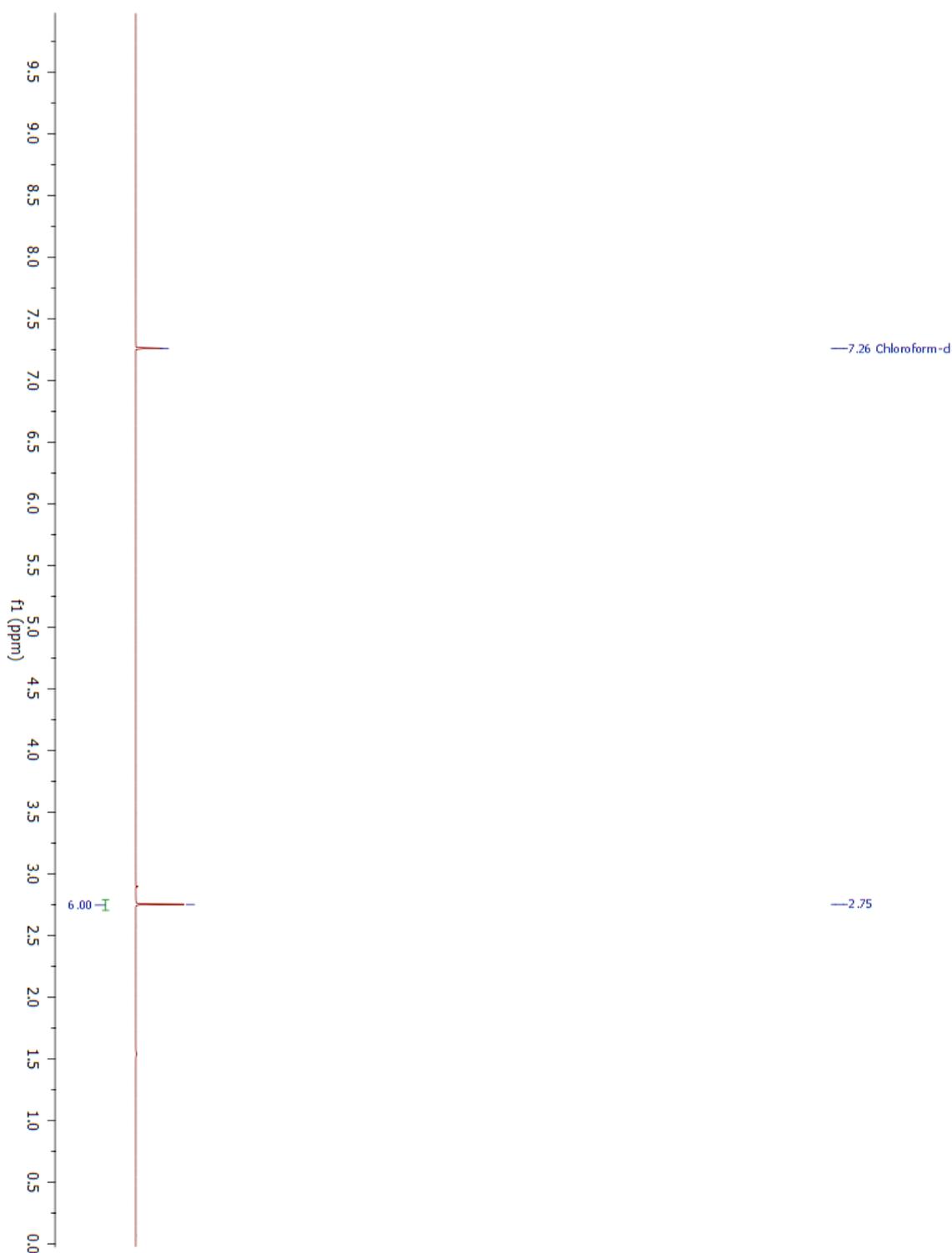
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# APPENDIX

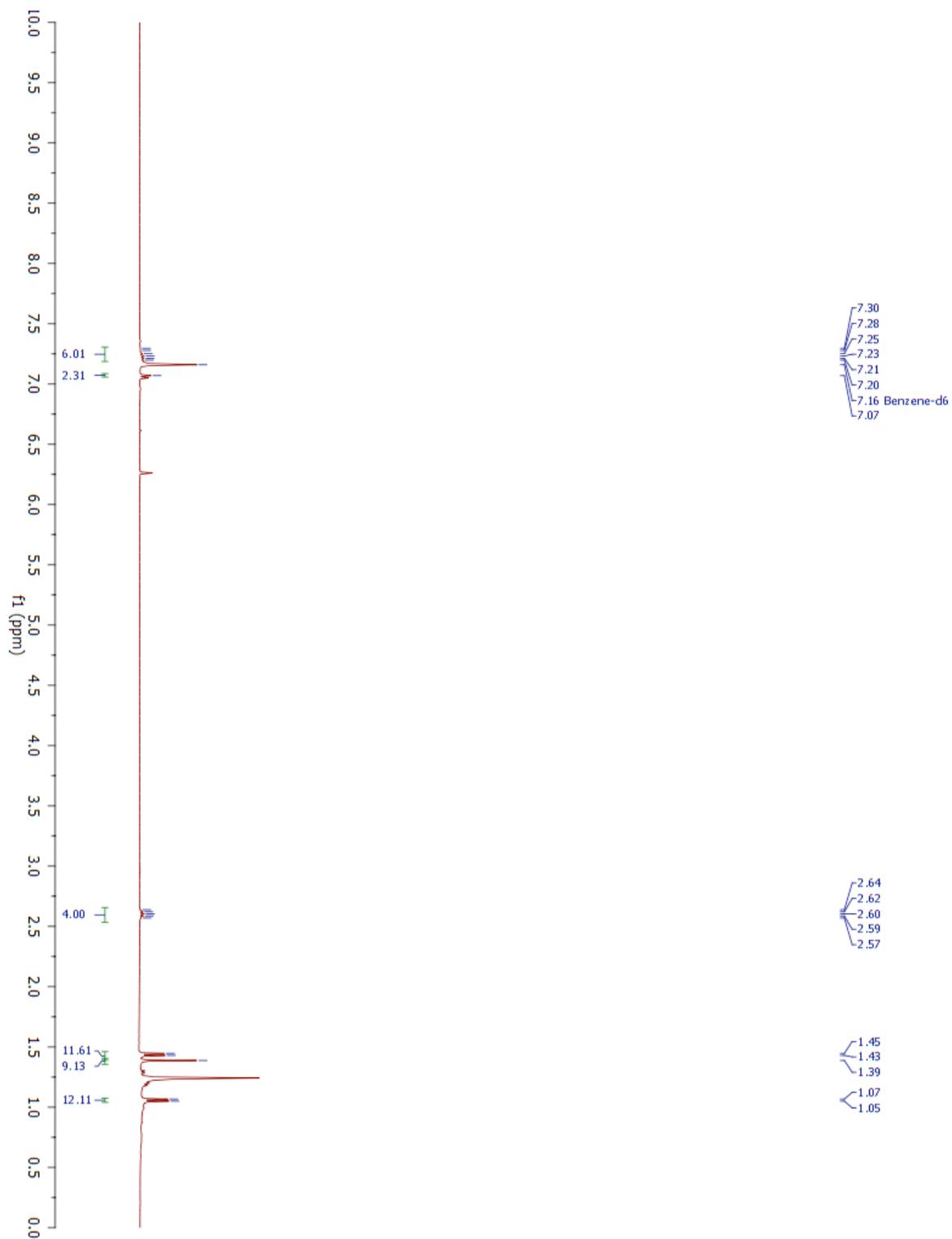
## 4.0 $^1\text{H-NMR}$ Spectroscopic Data for Gold(I) complexes

$\text{AuSMe}_2\text{Cl}$

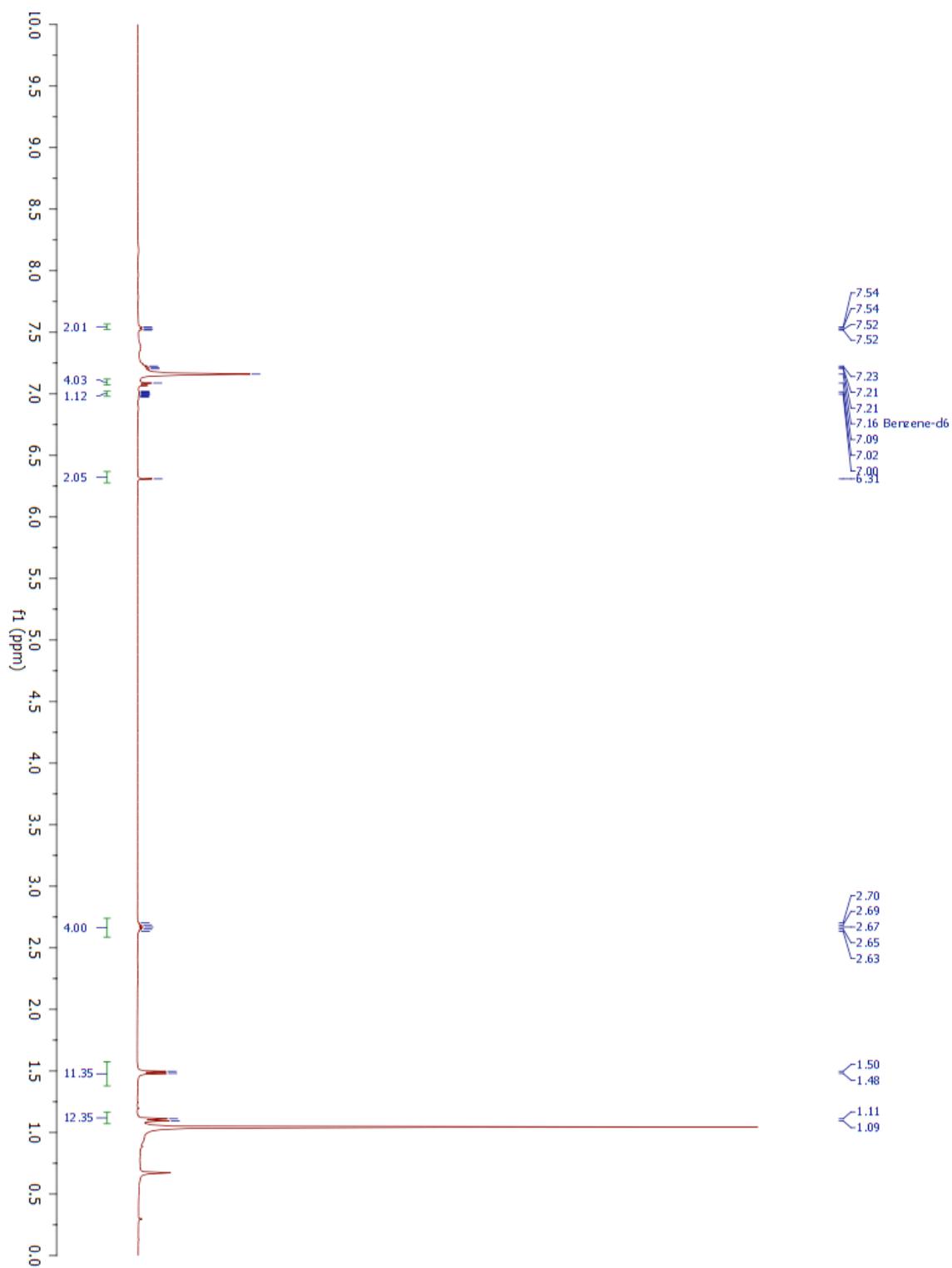
$\text{CDCl}_3$



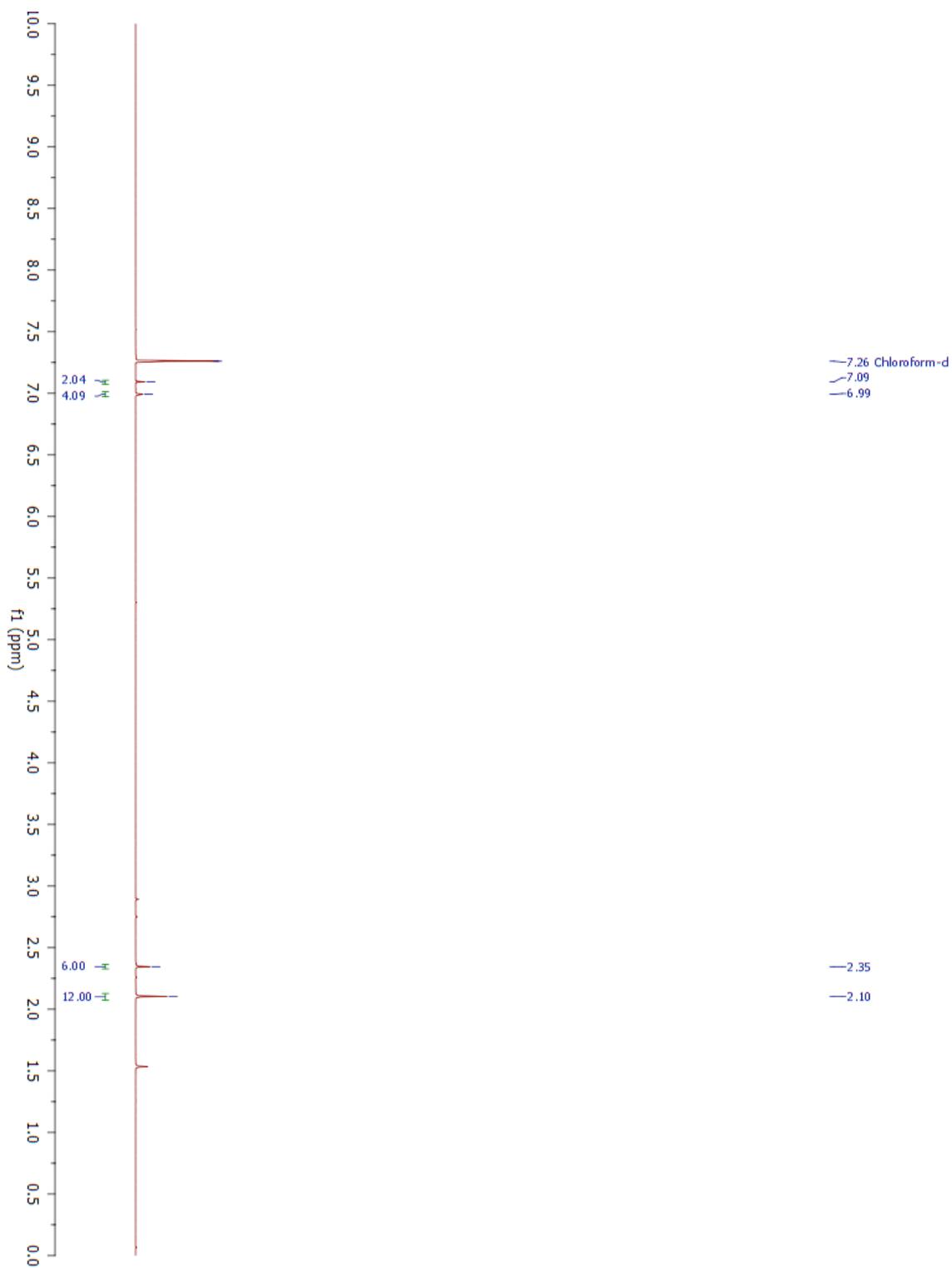
IPrAu-*t*-OBu  
d<sub>6</sub>-benzene



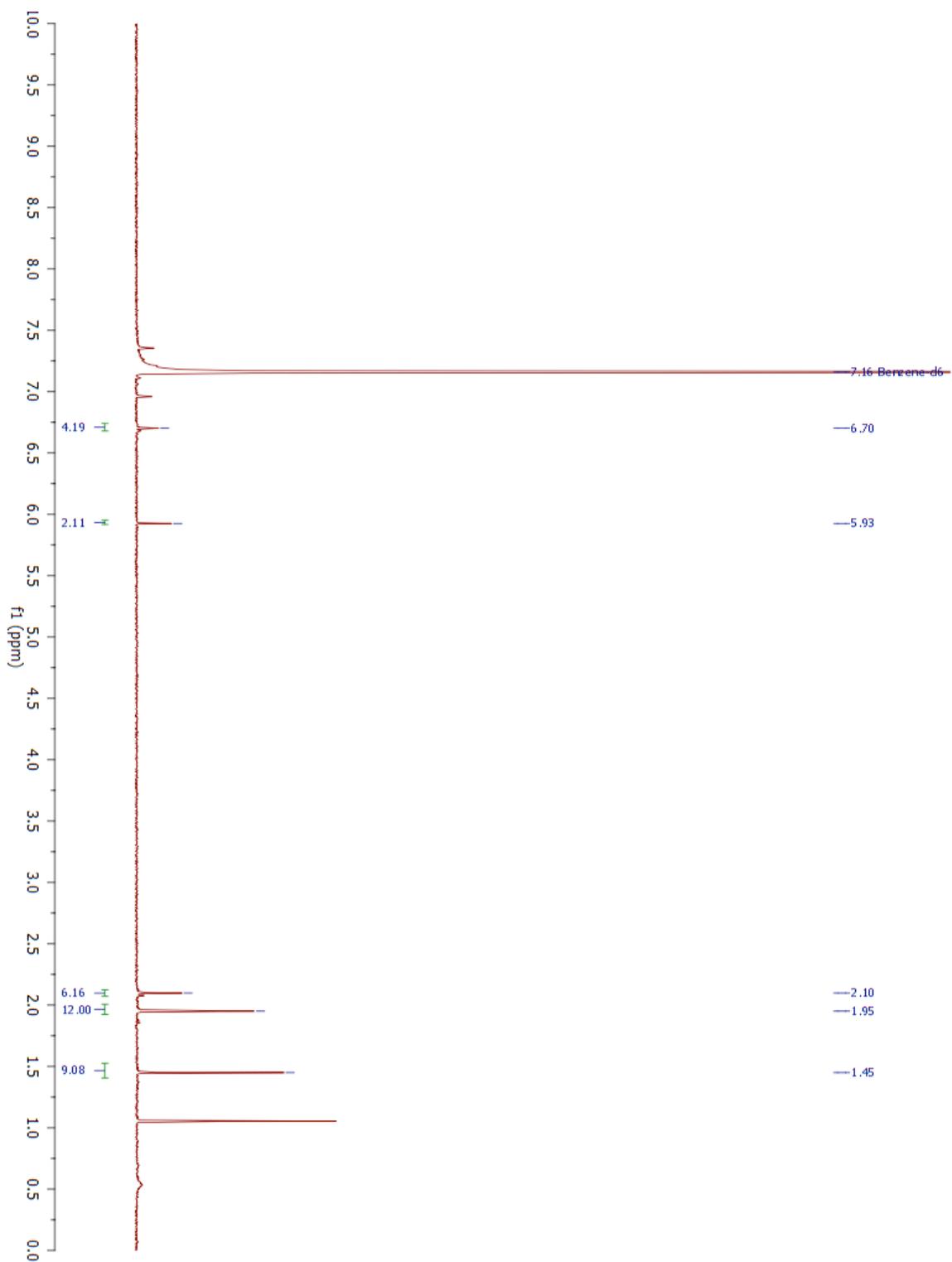
IPrAuPh  
d<sub>6</sub>-benzene



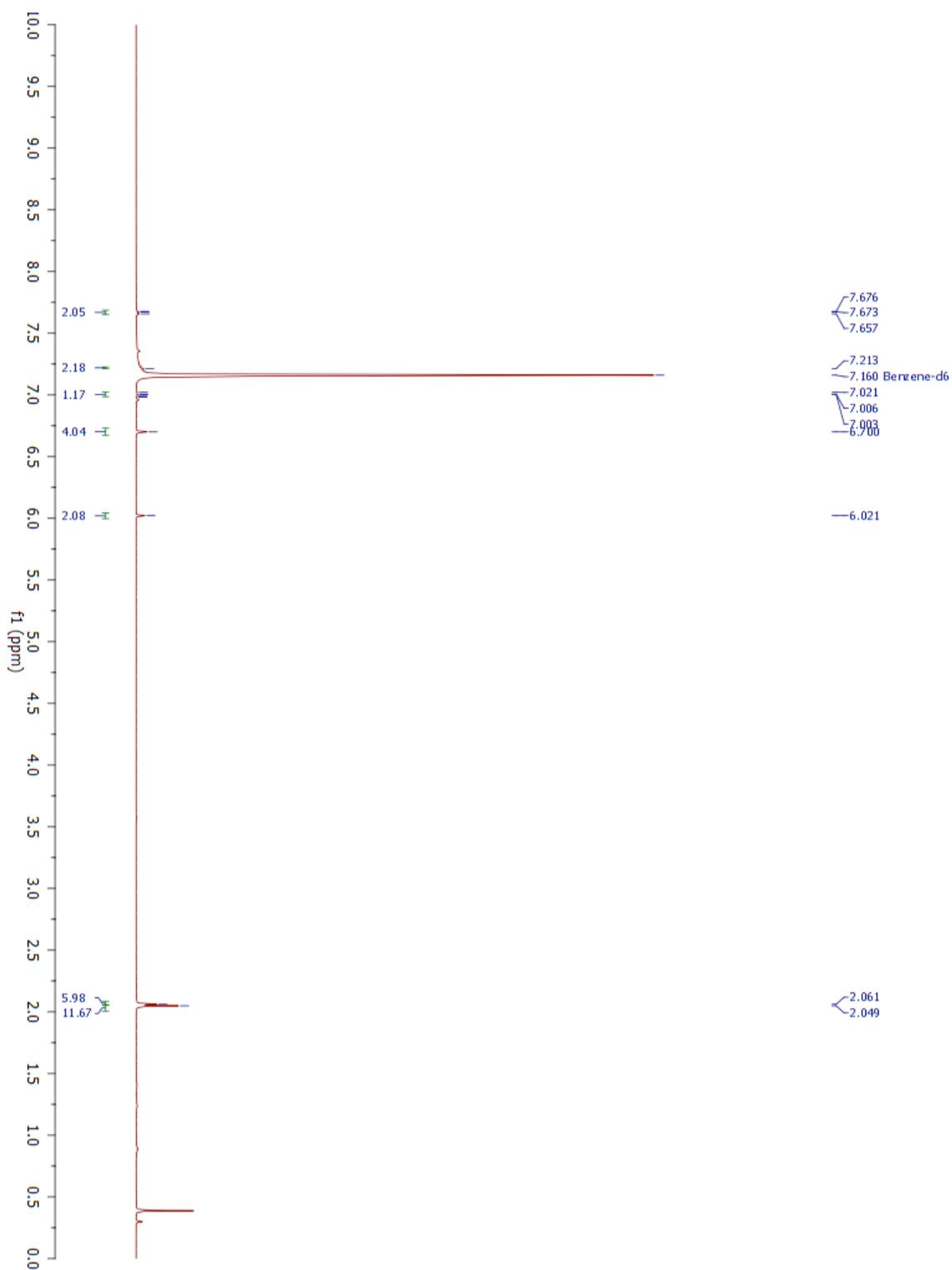
IMesAuCl  
CDCl<sub>3</sub>



IMesAuOtBu  
CDCl<sub>3</sub>



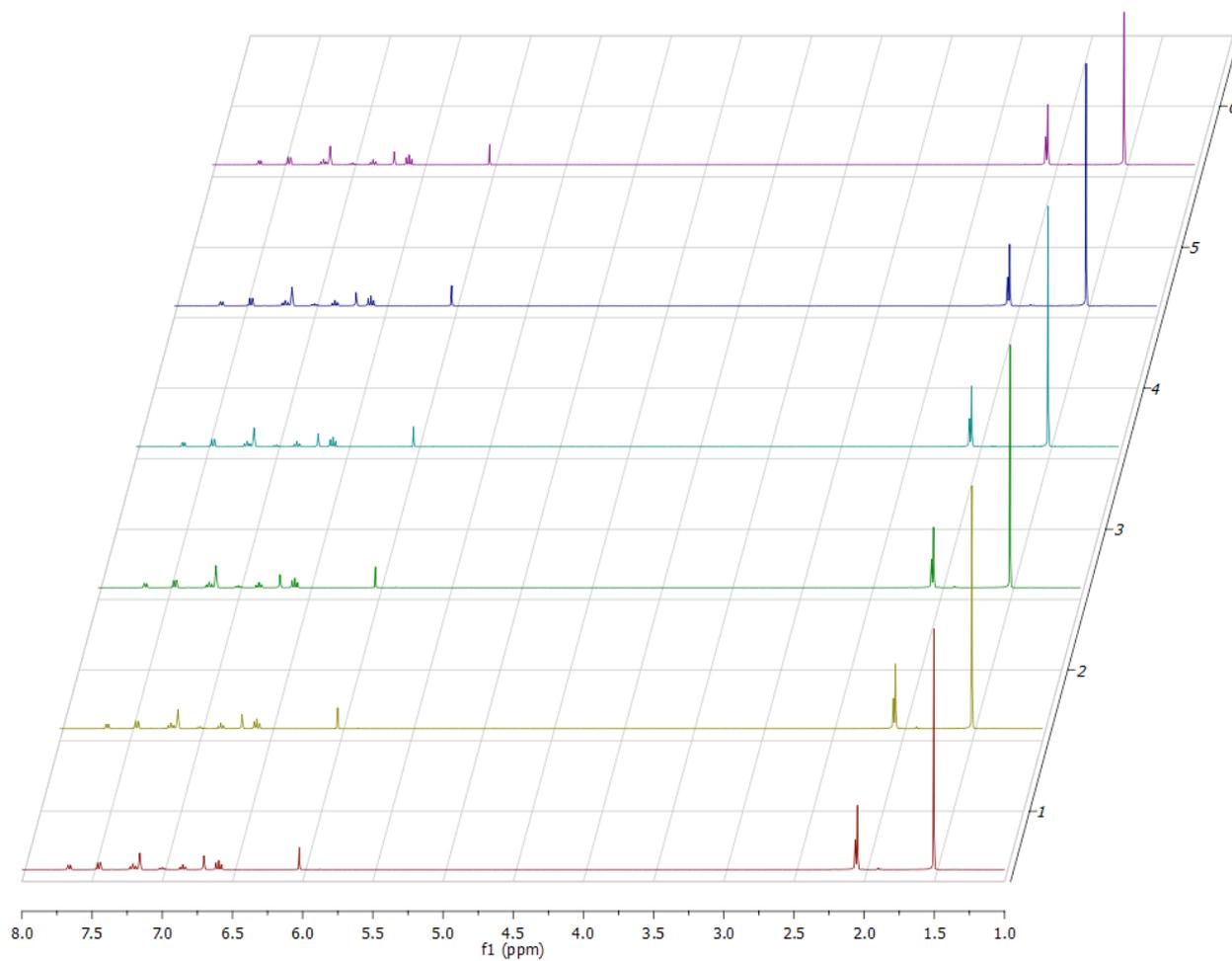
IMesAuPh  
d<sub>6</sub>-benzene



## 4.1 $^1\text{H}$ -NMR Spectroscopic Data for reactivity experiments

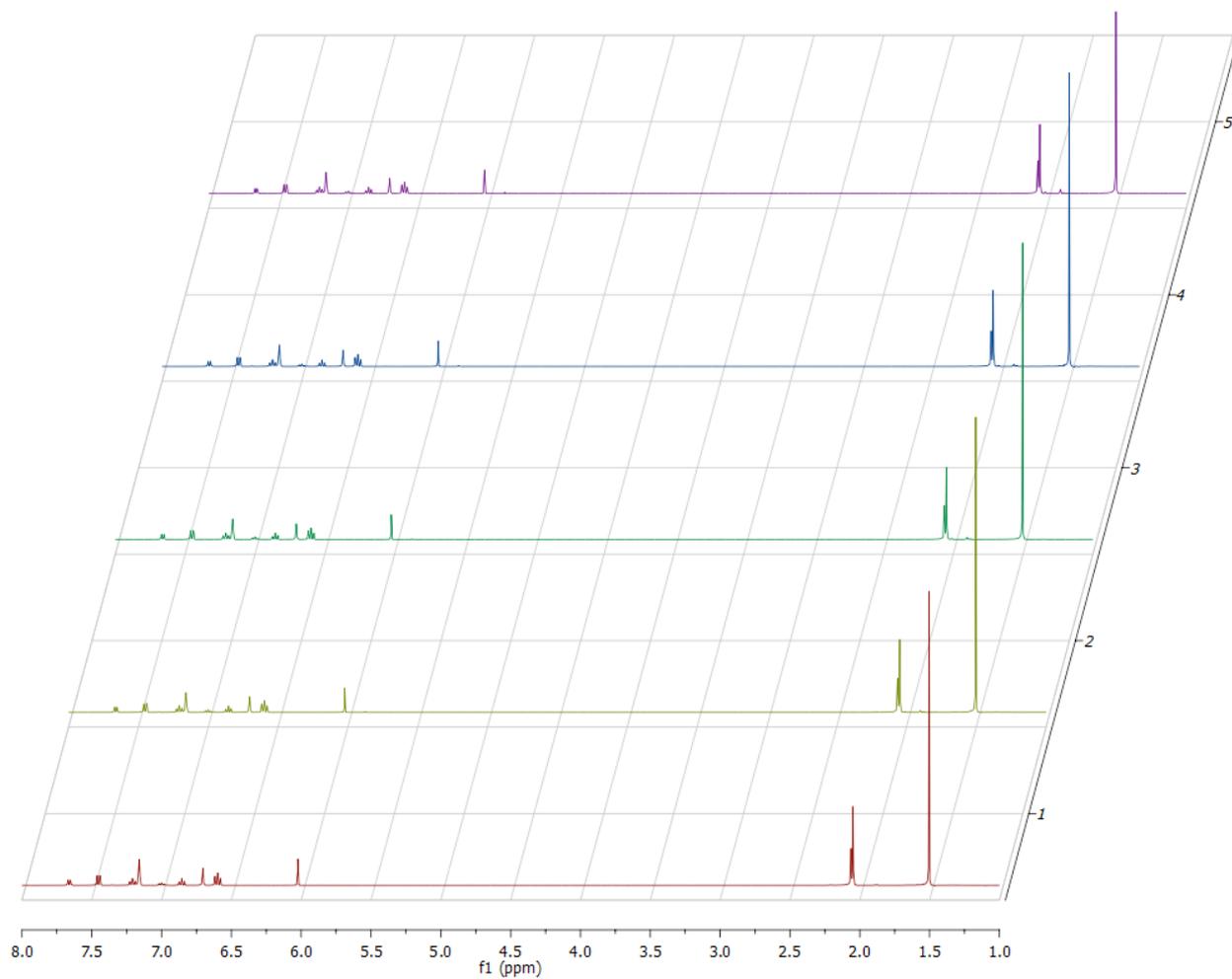
1<sup>st</sup> experiment

IMesAuPh + IS + PhI, 90°C: 1h. 2h. 5h. 21h. 47h, 137h, no additive



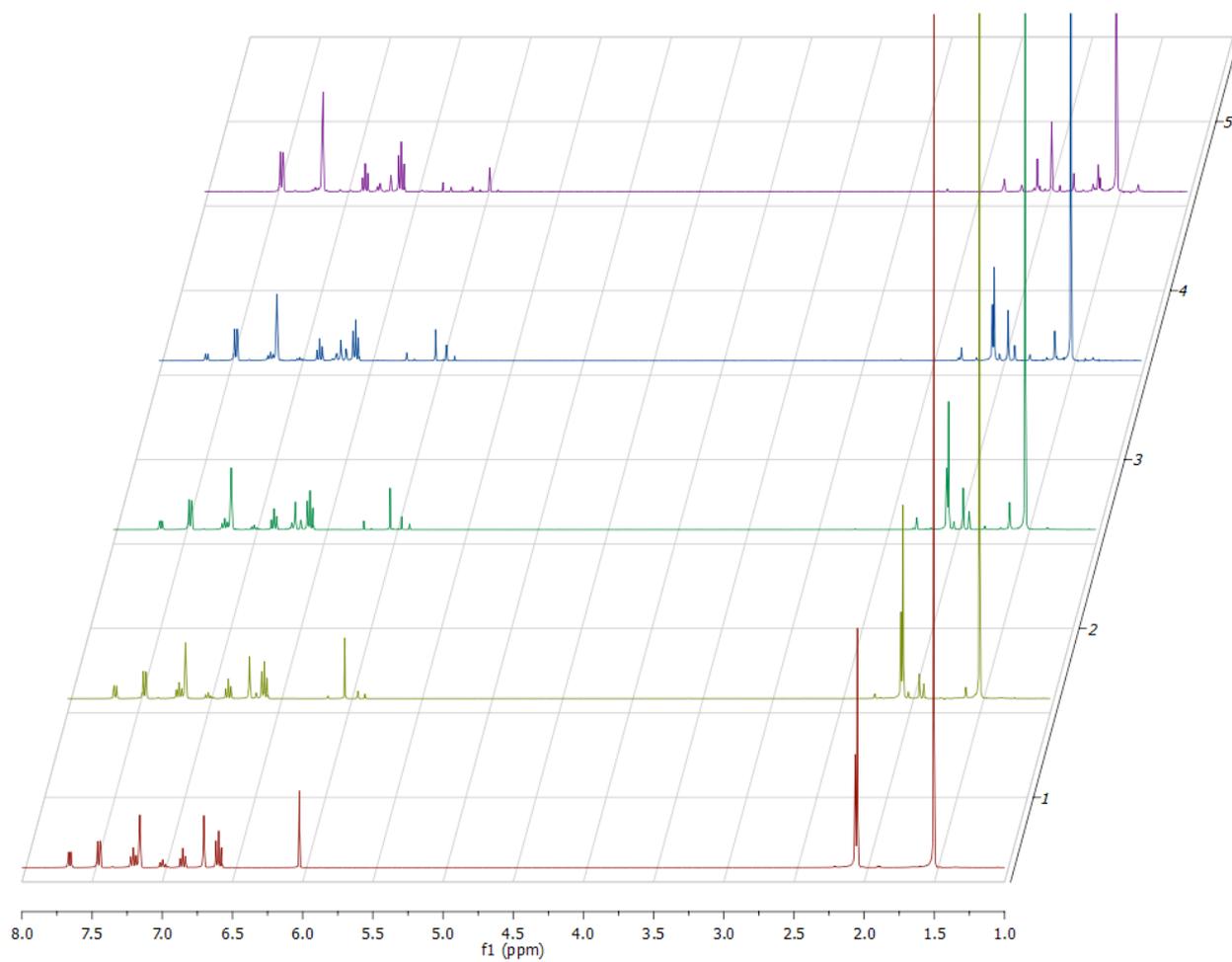
3<sup>rd</sup> experiment

IMesAuPh, IS, PhI, 110°C; 1h, 2h, 5h, 21h, 47h, no additive (reference experiment)



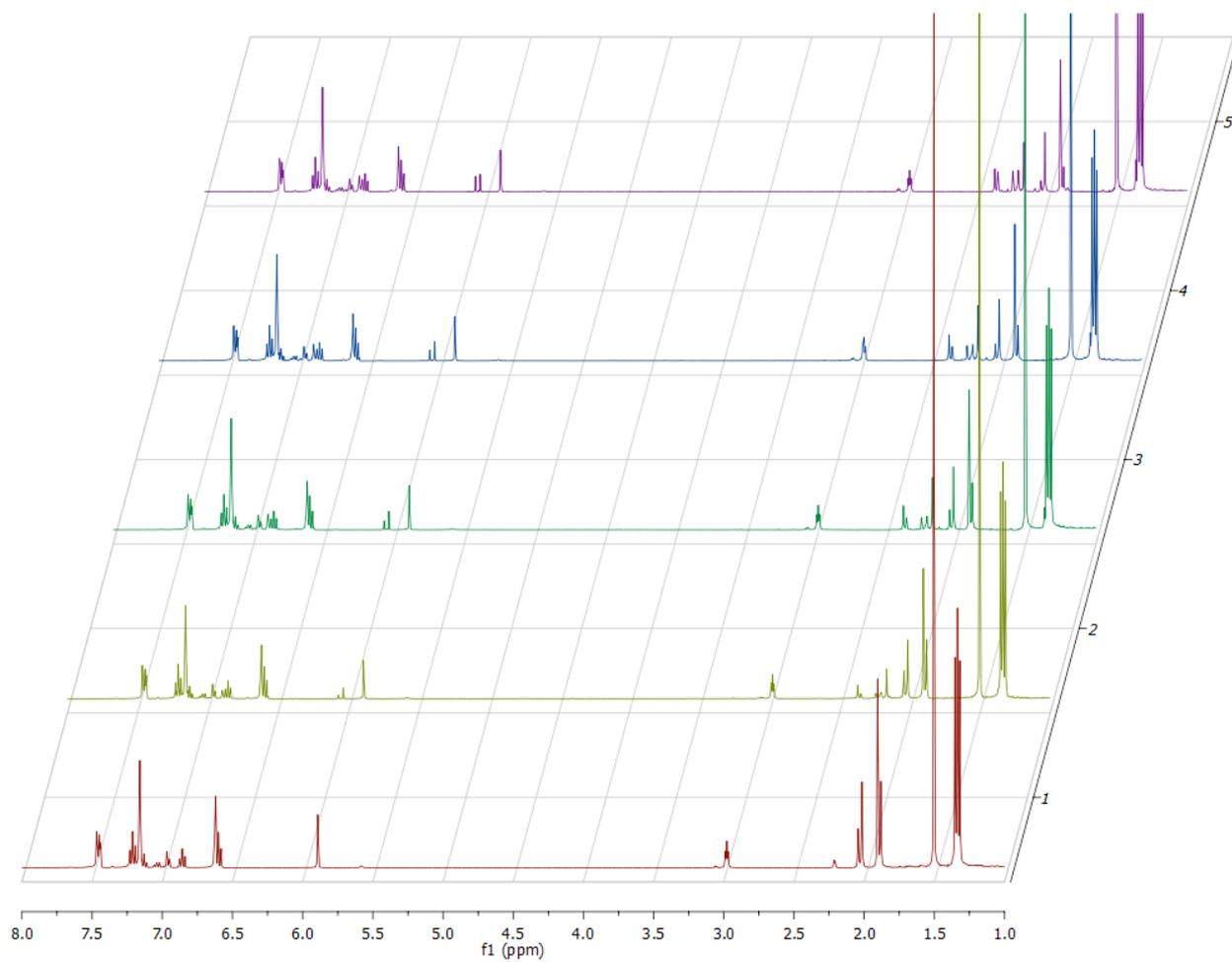
3<sup>rd</sup> experiment

IMesAuPh, IS, PhI, 1h, 2h, 5h, 21h, 47h, 110°C, CuI



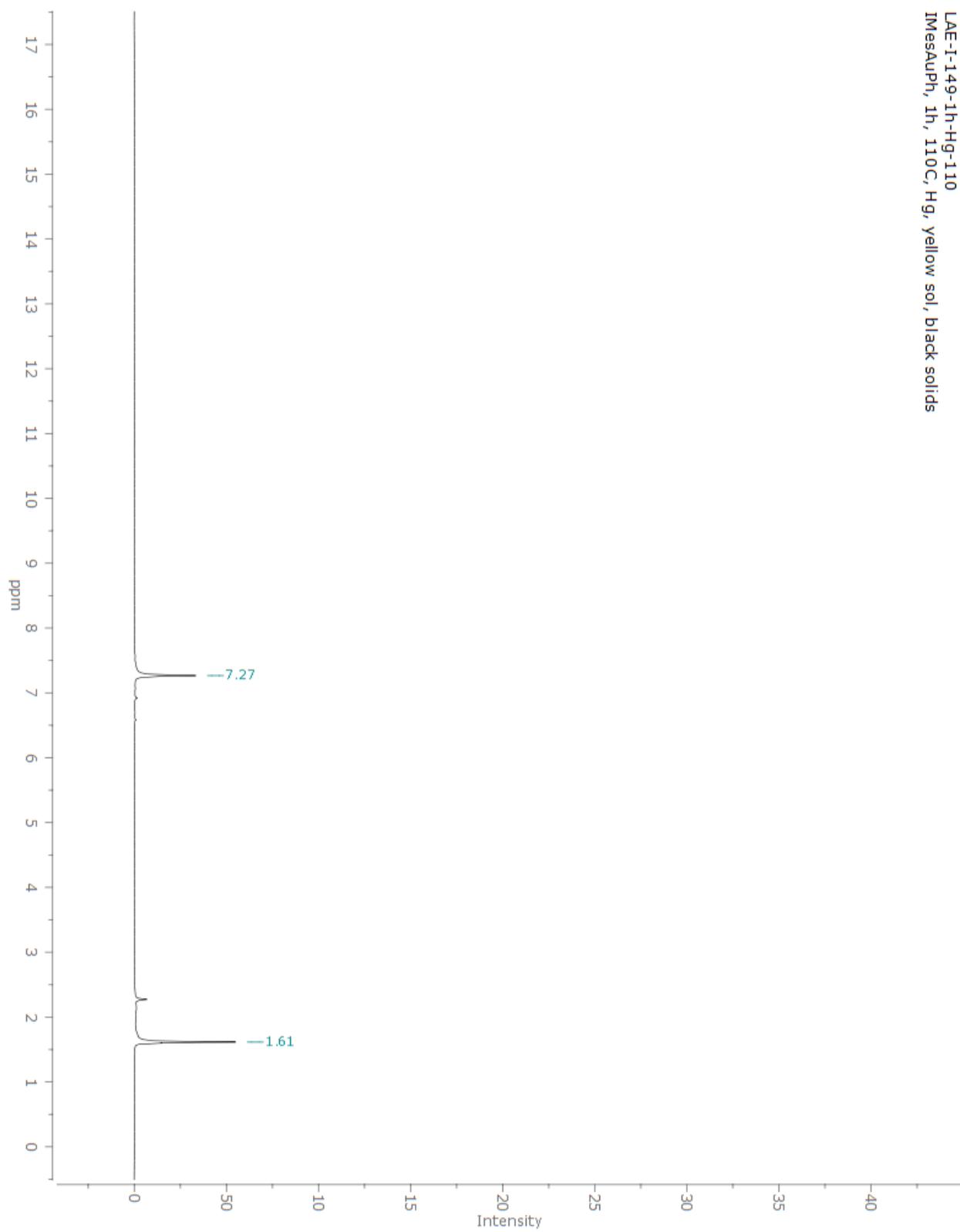
3<sup>rd</sup> experiment

IMesAuPh, IS, PhI: 1h, 2h, 5h, 21h, 47h, 110°C, PCP-PdCl



IMesAuPh, IS, PhI, 24h, 110°C, Hg(1) (Mercury droplet experiment)

LAE-I-149-1h-Hg-110  
IMesAuPh, 1h, 110C, Hg, yellow sol, black solids



## 4.2 Crystallographic data

**Table A1.** Crystallographic data for IMesAuPh.

Crystal data	
Chemical formula	C <sub>54</sub> H <sub>60</sub> Au <sub>2</sub> N <sub>4</sub>
Mr	224
Crystal system, space group	Triclinic, P-1
Temperature (K)	293
a, b, c (Å)	9.934 (3), 15.632 (4), 16.449 (4)
$\alpha$ , $\beta$ , $\gamma$ (°)	79.49 (2), 83.93 (2), 77.07 (2)
V (Å <sup>3</sup> )	2442.1 (11)
Z	2
Radiation type	Mo K $\alpha$
$\mu$ (mm <sup>-1</sup> )	2.99
Crystal size (mm)	0.38 × 0.34 × 0.23
Data collection	
Diffractometer	Oxford Diffraction CCD
$\mu$ (mm <sup>-1</sup> )	2.99
No. of measured, independent and observed [ $I > 3\sigma(I)$ ] reflections	18276, 10869, 7112
Rint	23
Refinement	
R[F <sub>2</sub> > 2 $\sigma$ (F <sub>2</sub> )], wR(F <sub>2</sub> ), S	0.030, 0.068, 1.12
No. of reflections	10869
No. of parameters	551
No. of restraints	0

**Table A2.** Crystallographic data for Au(SMe<sub>2</sub>)Cl

Crystal data	
Chemical formula	C <sub>2</sub> H <sub>6</sub> AuClS
$M_r$	294.5
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	293
$a, b, c$ (Å)	6.0298 (7), 14.8417 (18), 6.4169 (7)
$\beta$ (°)	95.702 (10)
$V$ (Å <sup>3</sup> )	571.42 (11)
$Z$	4
Radiation type	Mo $K\alpha$
$\mu$ (mm <sup>-1</sup> )	26.42
Crystal size (mm)	0.16 × 0.07 × 0.05
Data collection	
Diffractometer	Oxford Diffraction CCD
$\mu$ (mm <sup>-1</sup> )	26.42
No. of measured, independent and observed [ $I > 3\sigma(I)$ ] reflections	12812, 1417, 1165
$R_{\text{int}}$	0.045
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.023, 0.027, 1.20
No. of reflections	1417
No. of parameters	46
No. of restraints	0