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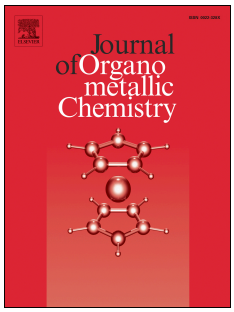

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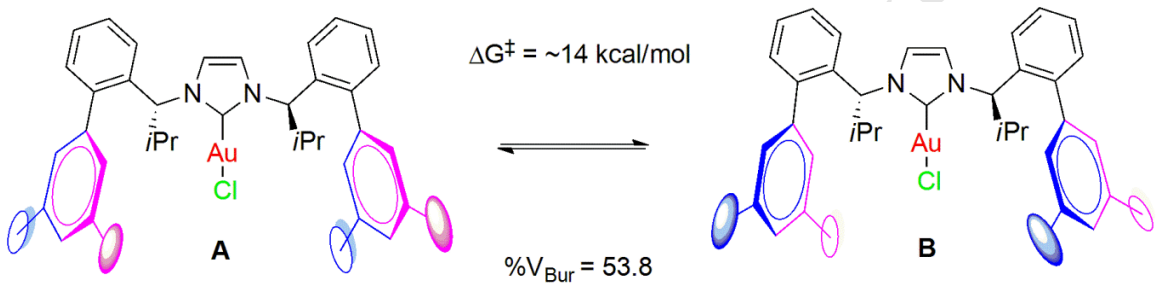
Graphical Abstract

Nine novel chiral [(NHC)Au(I)Cl] complexes are synthesized and characterized. The new chiral [(NHC)Au(I)Cl] complexes feature pairs of o-biphenyl substituents. The rotational barriers determined for the biphenyl C-C bond rotation in these complexes are greater than usual.



Synthesis and Characterization of Novel Chiral [(NHC)Au(I)Cl] Complexes: Featuring ortho-Biphenyl Substituents

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Abstract: A series of new chiral [(NHC)Au(I)Cl] are synthesized. The chiral NHC ligands feature pairs of ortho-biphenyl groups. The distal phenyl groups of the biphenyl substituents are varied from simple phenyl, 3,5-dimethylphenyl, to 3,5-di-t-butylphenyl. X-Ray structure analysis were performed for two such [(NHC)Au(I)Cl] complexes. High percent buried volumes were calculated for two novel chiral [(NHC)Au(I)Cl]complexes whose structure were solved by an X-ray analysis. The rotational motion in the biphenyl group is slow on the NMR time scale. Rotational barriers were determined using WINDNMR for two of the chiral gold complexes.

Key words: NHC ligands, gold (I) complexes, ligand dynamics, percent buried volumes, rotational barrier.

Introduction

The field of the N-heterocyclic (NHC) ligands in homogeneous catalysis has significantly expanded in the last two decades due to many advantages in their stability and structural variability.[1-3] Chiral NHC ligands are being developed to replace chiral phosphines for several transition metal complexes.[4-7] As shown in Figure 1, NHC ligands **1**-**3** with saturated imidazole ring allow for two chiral centers in the ring, and the "gearing" effect transmits the asymmetry to the coordination site.[4-7]

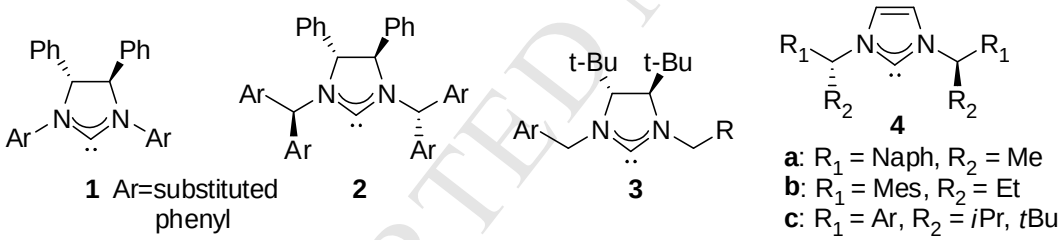

Figure 1. Representative chiral N-heterocyclic carbenes previously reported.

One of the earliest reported chiral NHCs has a core structure of imidazole (**4**) with varying substituents of R_1 and R_2. Herrmann and coworkers prepared the chiral NHC **4a** for a Rhodium complex.[8] Later Alexakis and coworkers were able to extend the usage to Cu-catalyzed conjugate additions with similar chiral NHCs.[9] Saito reported a three component Ni-catalyzed reaction with chiral NHC ligand **4b**.[10] At the same time, Kundig found that **4c** with a *t*-butyl group as the substituent R_2 and variations at the aryl substituent R_1 provided an effective chiral NHC ligand for a Pd-catalyzed C-H activation reaction.[11]

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During our study of intramolecular [4+3] cycloadditions, we discovered that gold complexes with NHC ligands are most suitable for such transformations.[12] Gold complexes with chiral NHC ligands are relatively new and have only begun to appear recently. The tendency of gold(I) to form linear two-coordinate complexes makes the design of new chiral NHC ligands limited to mono dentate NHCs. The two coordination sites allow one mono dentate ligand and one coordination site for substrate. This limitation increases the challenge for the development of enantioselective catalysts. Our initial attempt in 2010 at the preparation of chiral NHC ligands for Au(I) complexes (Figure 2, **5** and **6**) revealed the importance of the ligand structure on gold complex stability.[13] Complexes **5** and **6** were activated for the cyclopropanation reactions of propargyl esters upon treatment with a silver salt. However, their thermal stability is much less robust compared to Nolan's achiral complex Au(IPr)Cl.[14] The lesson we learned was that the design of chiral NHC ligands for preparing gold catalysts must take into account the steric bulk of the ligand to protect the gold atom. Some of the more successful chiral [(NHC)Au(I)Cl]complexes are from the groups of Tomioka and Kundig, independently.[15, 16]

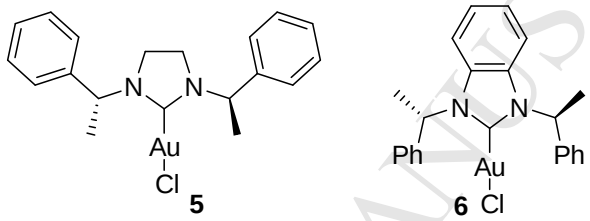


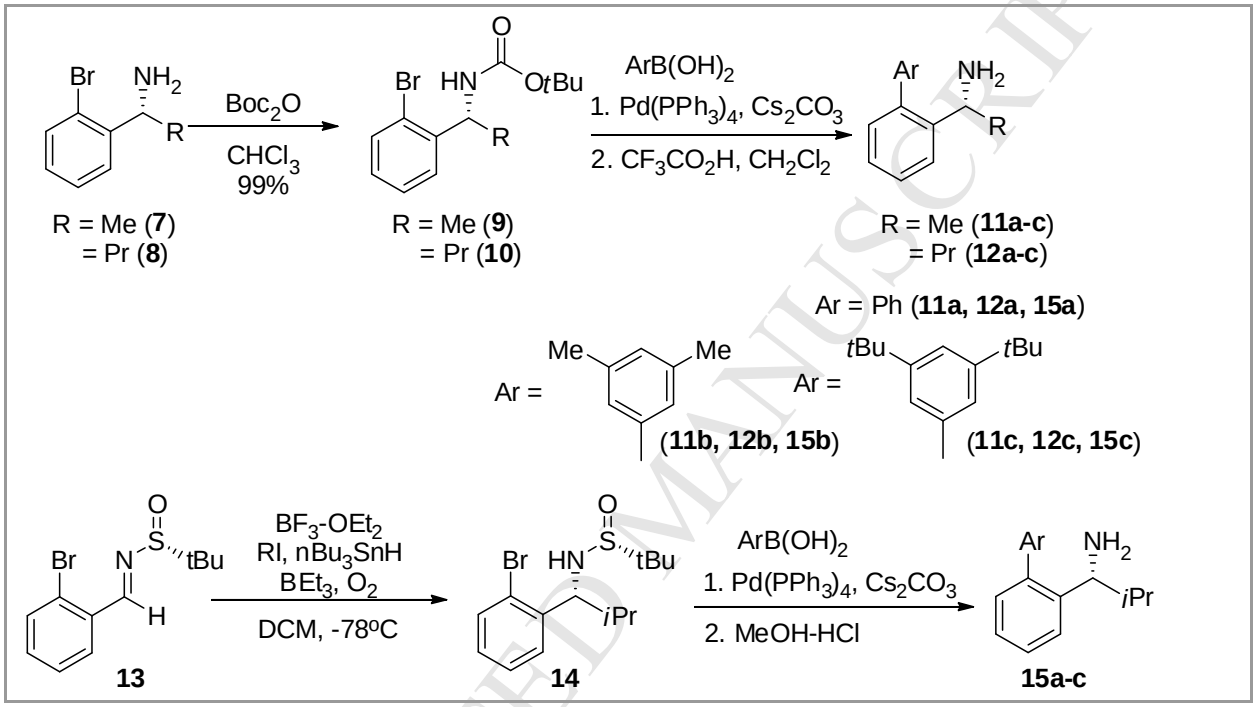
Figure 2. Thermally labile chiral [(NHC)Au(I)Cl] complexes previously reported by us.[13]

Our continued interest in improving NHC ligands so that it will be suitable for Au(I) catalysis with cycloaddition reactions led us to choose the unsaturated NHC as the core structure (**4**). We surmised that the substituents on nitrogen atoms can be further improved so that a strong steric bias would occur when coordinated to Au(I). Thus far the groups of Alexakis,[17] Saito,[10] and Kundig[18] have modified NHC **4** by changing the alkyl and aryl groups with varying degree of success. The alkyl group variations include methyl, ethyl, isopropyl, and t-butyl, while the aryl groups employed so far were phenyl, naphthyl, mesityl, and 2-methylphenyl and 2-methoxyphenyl groups.[19] Kundig's group did most work in this area including a chiral ligand with a *p*-biphenyl substituent.[16] The difference between the chiral NHC reported in this study and the one example from Kundig's group is the position where the biphenyl attaches to the chiral center. We have ortho-biphenyl substitution while one example of a para-biphenyl was reported previously.

Results and discussion

In our design, both stability and steric bias are aimed for the NHC ligand. Thus both steric and electronic effects need to be considered. The important key element in the new design is a bulky o-biphenyl group as the aryl substituent. Buchwald and co-workers were the first to use a biphenyl *o*-(di-*tert*-butylphosphino) palladium complex in the catalysis of Suzuki coupling reactions.[20, 21] The same biphenyl phosphino ligand was then used for Au catalysts by Echavarren.[22] Favorable metal-pi interactions have been reported in transition metal complexes.[23, 24] The ligand containing the o-biphenyl moiety appears to provide a favorable scaffold for such stabilizing interactions. To the best of our knowledge, none of the effective N-heterocyclic carbene ligands reported so far has incorporated the o-biphenyl group.[7, 25] As depicted in Scheme 1, the ortho aryl groups in two ligand series are further

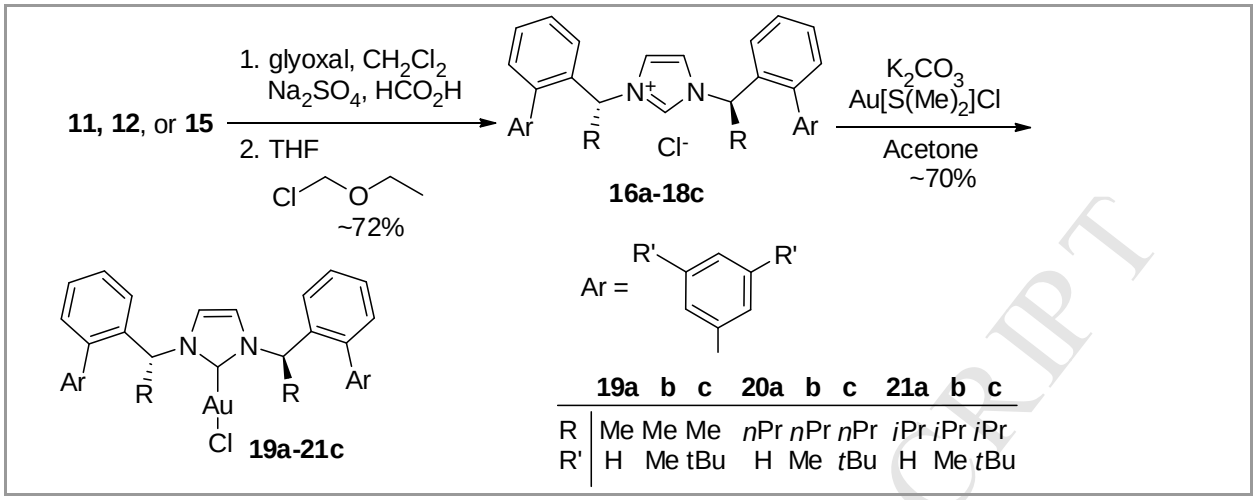
adorned with 3,5-dialkyl (methyl or t-butyl) group. The alkyl groups (R) at the stereocenter vary in size from a methyl group to an isopropyl group. Using this modular approach, a total of nine chiral amines (**11a-12c**, and **15a-c**) with unique structures are prepared. We employed the known chiral amines **7** and **8** as the starting materials for the desired amines **11a-12c**, Scheme 1.[26, 27] The protection of the amino function in **7** and **8** using t-butoxycarbonyl (t-BOC) enabled Suzuki coupling with three different aryl boronic acids. After Suzuki coupling, the removal of the t-BOC with CF_3CO_2H produced chiral amines **11a-12c**.



Scheme 1 Synthesis of chiral amines **11a-12c** and **15a-c** with ortho-biphenyl groups via Suzuki coupling reactions.

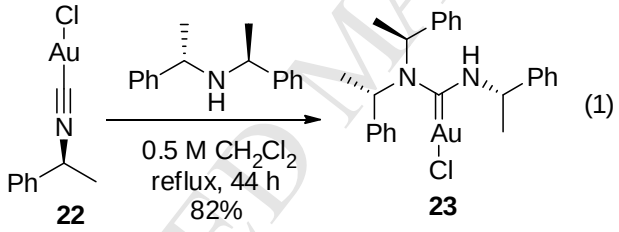
Chiral amines **15a-c** were prepared efficiently through intermolecular alkyl radical addition starting from the known sulfonamide **13**, Scheme 1.[28, 29] We were pleased to observe smooth Suzuki coupling reactions of the sulfonamide **14** with different $ArB(OH)_2$, which eliminated the need of using an amino protecting group. The sulfinyl group of **14** was removed with acidic methanol after Suzuki coupling to afford chiral amines **15a-c**.

The chiral Au(I) complexes **19a-21c** are prepared as shown in Scheme 2 following the improved procedure by Nolan and co-workers.[30] Briefly the chiral amines (**11, 12**, or **15**) are converted to diimine intermediates by treating with glyoxal and formic acid. The resulting diimines were immediately allowed to react with chloromethyl ethyl ether to produce the imidazolium chlorides (**16a-18c**). The chiral NHC-gold(I) complexes (**19a-21c**) were obtained by stirring the imidazolium chloride with $Au[S(Me)_2]Cl$ in acetone in the presence of K_2CO_3. The gold(I) complexes of **19a-21c** are stable and can be purified by column chromatograph. All of their structures are carefully studied by ^1H and ^{13}C NMR spectroscopy.

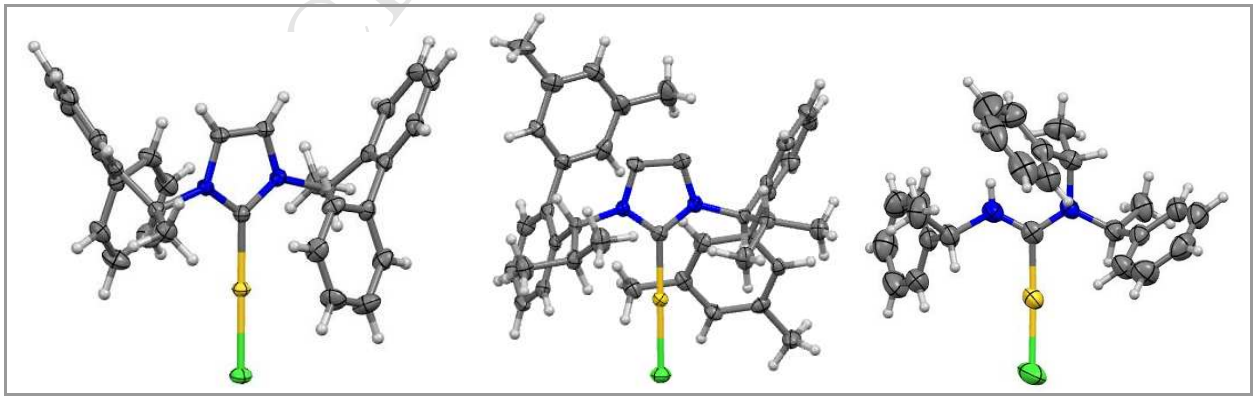


Scheme 2 Synthesis of Au(I) complexes **19a-21c** with variations at the alkyl (R) and the aryl (Ar) groups.

For comparison purpose, we prepared the [(ADC)Au(I)Cl] complex (**23**) from the known isonitrile **22**[31] as shown in eq. 1.[32] An X-ray structure analysis of **23** is shown in Figure 3. The key structural data for the [(ADC)Au(I)Cl] complex (**23**) are compiled in Table 1 along with the NHC-AuCl complexes.



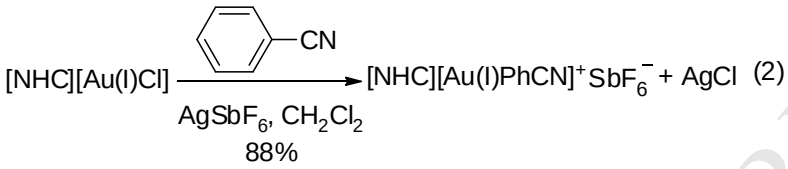
X-Ray quality crystals were also obtained for two of the NHC complexes (**19a** and **21b**) when the purified [NHCAu(I)Cl] complexes were dissolved in a minimal amount of dichloromethane in a long test tube and hexanes were carefully layered on top of the solution. ORTEP representations of [NHC][AuCl] (**19a** and **21b**) and [ADC][AuCl] (**23**) are presented in Figure 3.



19a **21b** **23**

Figure 3. ORTEP representation of [NHC][AuCl] (**19a** and **21b**) and [ADC][AuCl] (**23**).

We are pleased to find that the new chiral gold(I) complexes (**19a-21c**) can produce catalysts that are much more stable than those we have previously reported, i.e., catalysts prepared from complexes **5** and **6** or **23**. To avoid unpredictable effects of the silver salt, we usually try to minimize the presence of the silver salt by protecting Au(I) with benzonitrile after abstraction of the chloride with $AgSbF_6$ and filtering off the resulting AgCl, eq. 2.[12, 33]



Upon the chloride abstraction by using $AgSbF_6$, the cationic Au(I) complexes are active catalysts and are susceptible to disproportionation reaction leading to "gold mirroring".[13] However the complexes prepared in this study (Scheme 2) appear to be stable for days after the chloride abstraction treatment as shown in eq. 2. In order to compare their thermal stability, variable temperature NMR experiments were performed on the two different Au(I) complexes, the $[NHC][Au(I)PhCN]^+SbF_6^-$ complex prepared from **21b**, and the $[ADC][Au(I)PhCN]^+SbF_6^-$ complex prepared from **23**. Each gold complex was treated with an equal molar amount of $AgSbF_6$ and PhCN in $CDCl_3$ and stirred at room temperature for 15 min, eq. (2).

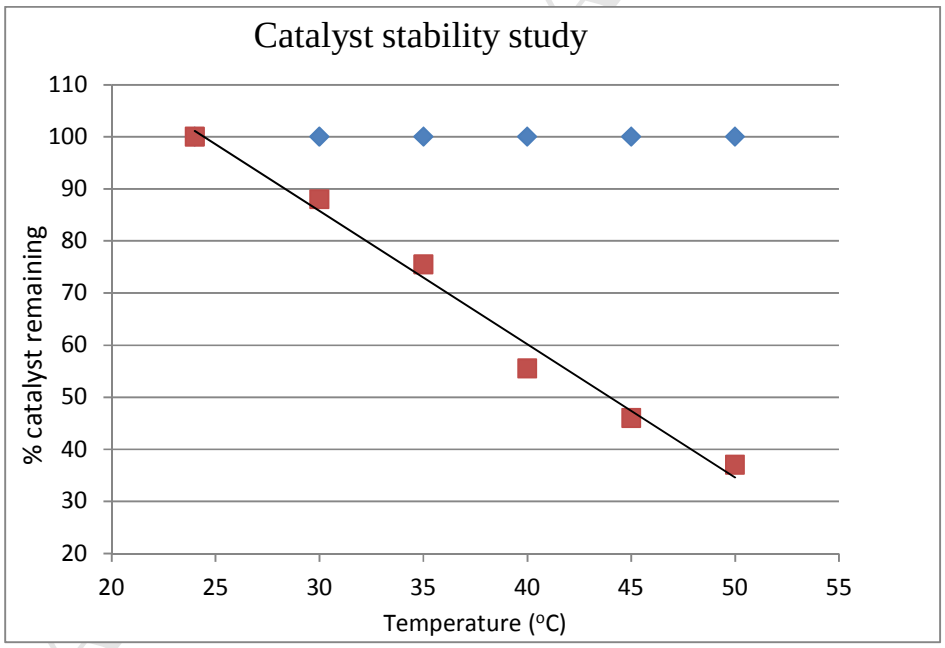


Figure 4. Catalyst stability study: (♦) catalyst prepared from **21b**, (■) catalyst prepared from **23**.

The resulting suspension was filtered and the filtrate was loaded into an NMR tube and the ^1H NMR spectra were recorded at 30 min interval from room temperature to 50 °C. The ^1H NMR spectra of the cationic Au(I) complexes were recorded from rt to 50 °C during a five hour time period. The $CDCl_3$

we used was purchased and used as received. The one equivalent of PhCN serves to stabilize the cationic gold complex in solution. The cationic catalyst prepared from **21b** showed no signs of change from room temperature to 50 ºC and from the first to the last spectrum taken during the 5 hours of time, Figure 4.

For catalyst prepared from **23**, it was convenient to monitor the ortho protons on one of the phenyl groups during the NMR study because of their up-field chemical shifts. A steady decrease of the peak at 6.6 ppm was observed as the temperature rises. At the conclusion of the experiments for catalyst **23**, a gold mirror was deposited onto the bottom of the NMR tube. Thus the variable temperature NMR experiments carried out with the two gold complexes support the hypothesis that the o-biphenyl substituent protect the cationic Au(I) catalyst in the $[NHC][Au(I)PhCN]^{+}SbF_6^{-}$ complex prepared from **21b**.

It is interesting and informative to compare their properties with what we have reported previously in order to understand the important elements in [(NHC)Au(I)Cl] structures. Both steric and electronic effects of the ligands in metal complexes play a role in the property of the complex. In gold(I) complexes, steric effects appear to be extremely important. One likely reason is that the steric bulk of the ligands can protect the Au atom from disproportionation reaction, hence leading to improved thermal stability. The evaluation of ligand steric effects has been developed for both phosphines and NHCs. Tertiary phosphine ligands are commonly classified using the Tolman cone model for steric effects around metal center.[34] Nolan and Cavallo proposed an alternate model, initially intended to measure the NHC steric bulk.[35, 36] The "percent buried volume", $\%V_{Bur}$ gives a measure of the space occupied by an organometallic ligand in the first coordination sphere of the metal center. The sphere has a defined radius and has the metal center at the core. $\%V_{Bur}$ is calculated using crystallographic data. A website named SambVca has been set up for the calculations of the percent buried volume.[37] By definition the bulkier a specific ligand is, the larger the amount of the sphere that will be occupied by the ligand, i.e. greater $\%V_{Bur}$. The relative significance of $\%V_{bur}$ was found to be more important in gold and silver complexes than in [PdCl(NHC)(allyl)] complexes.[38] The linear geometry of the silver and gold complexes was suggested to be at the origin of these differences.

Table 1. Comparison of Au-C bond length, C-Au-Cl bond angle and $\%V_{Bur}$ for [LAu(I)Cl] complexes.

Complex	Au-C1 (Å) Bond length	C-Au-Cl (°) Bond angle	C(Ar)--Au (Å) Close contact	$\angle_{CCCC}$ (°) Aryl-aryl torsion	$\%V_{Bur}$ [a]
IPrAuCl[b]	1.942(3)	177.0(4)	na	na	44.5
5[c]	1.998(3)	178.1(4)	na	na	36.4
6[c]	2.003(3)	179.5(4)	na	na	29.4
23[d]	2.004(3)	177.9(4)	3.73	na	36.7
19a	1.979(3)	180.0(4)	4.00	65.7	44.6
21b	1.989(3)	179.1(4)	3.36	66.8	53.8

[a] Parameters used for SambVca calculations: sphere radius, 3.50 A; Au-C1, 2.00 Å; mesh spacing, 0.10;

Bondi radius, 1.17. H atoms are excluded.

[b] Taken from Ref. [36]. [c] Work reported in Ref. [13]. [d] Taken from Ref.[32]

The values of $\%V_{Bur}$ were calculated for Au(I) complexes **5**, **6**, **19a**, **21b** and **23** and comparison is made to the steric demanding complex IPrAuCl.[39] The exact values of the $\%V_{Bur}$ also depend on the choice of several parameters: the sphere radius defined for the metal complex, the metal ligand bond distance, and a scale constant (bondi radius). In order to obtain consistent results, one should be careful to keep the same set of variables for all calculations. We employed the standard constant set reported by Nolan and the resulting percent buried volumes calculated are shown in Table 1, which include all gold(I) complexes that we have crystallographic data.

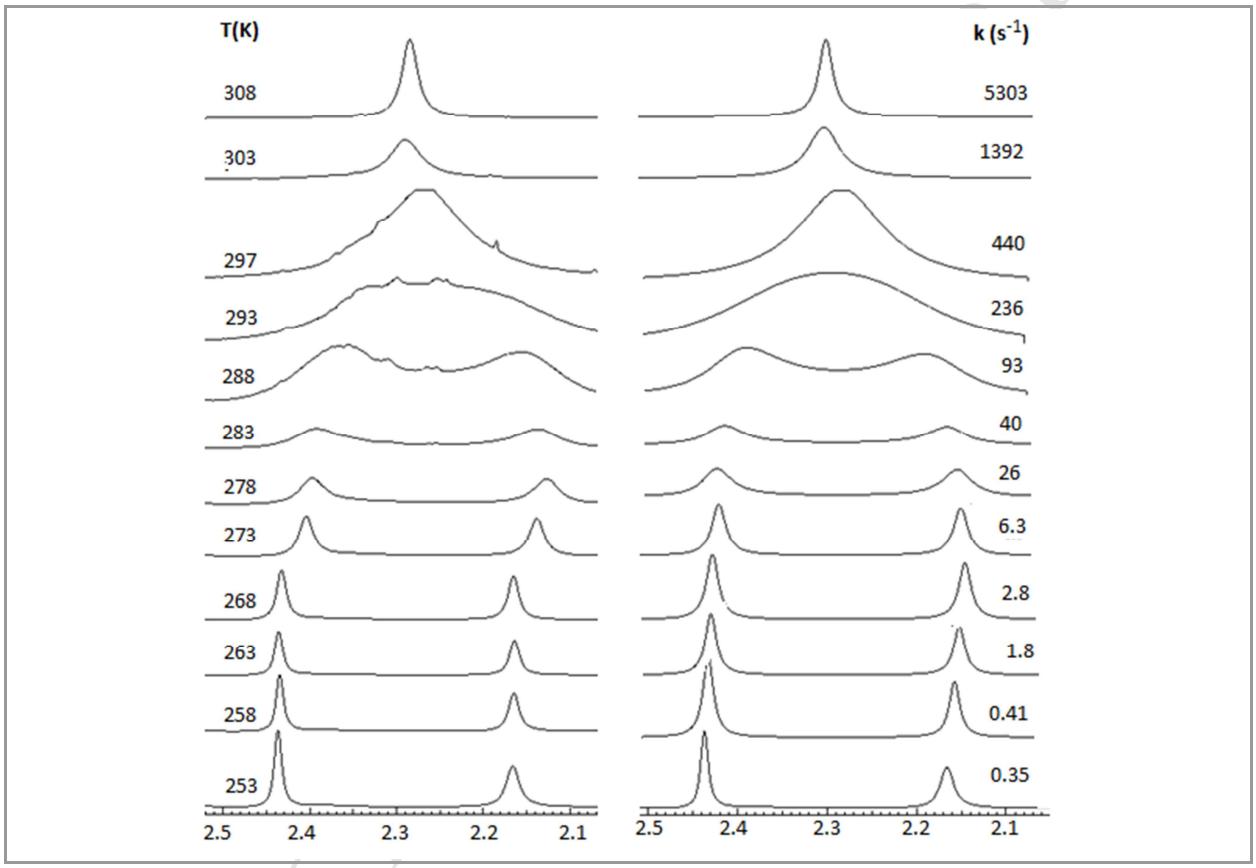


Figure 5. Left: temperature-dependent NMR signals (300 MHz in $CDCl_3$) of the 3,5-dimethyl protons on the distal phenyl group of compound **21b**. Right: computer simulations using a line shape analysis program (WINDNMR)[40] with the rate constants reported.

There is a remarkable correlation between the calculated $\%V_{Bur}$ and the Au(I) catalyst stability. Nolan's IPrAu(I)Cl complex has a value of 44.5 and is known to generate an extraordinarily stable catalyst. Our previously reported complex **6** has the smallest $\%V_{Bur}$ value of 29.4 in Table 1 and it was the least stable catalyst. Once the chloride is removed, complex **6** immediately decomposed about 50% when the NMR sample was run.[13] Complex **5** has a percent buried volume of 36.4 and it showed more stability than **6**, but it also decomposed within a few hours after activating with $AgSbF_6$.[13] The ADC complex **23** has a similar $\%V_{Bur}$ to **5** and it showed very similar stability as a catalyst.[32]

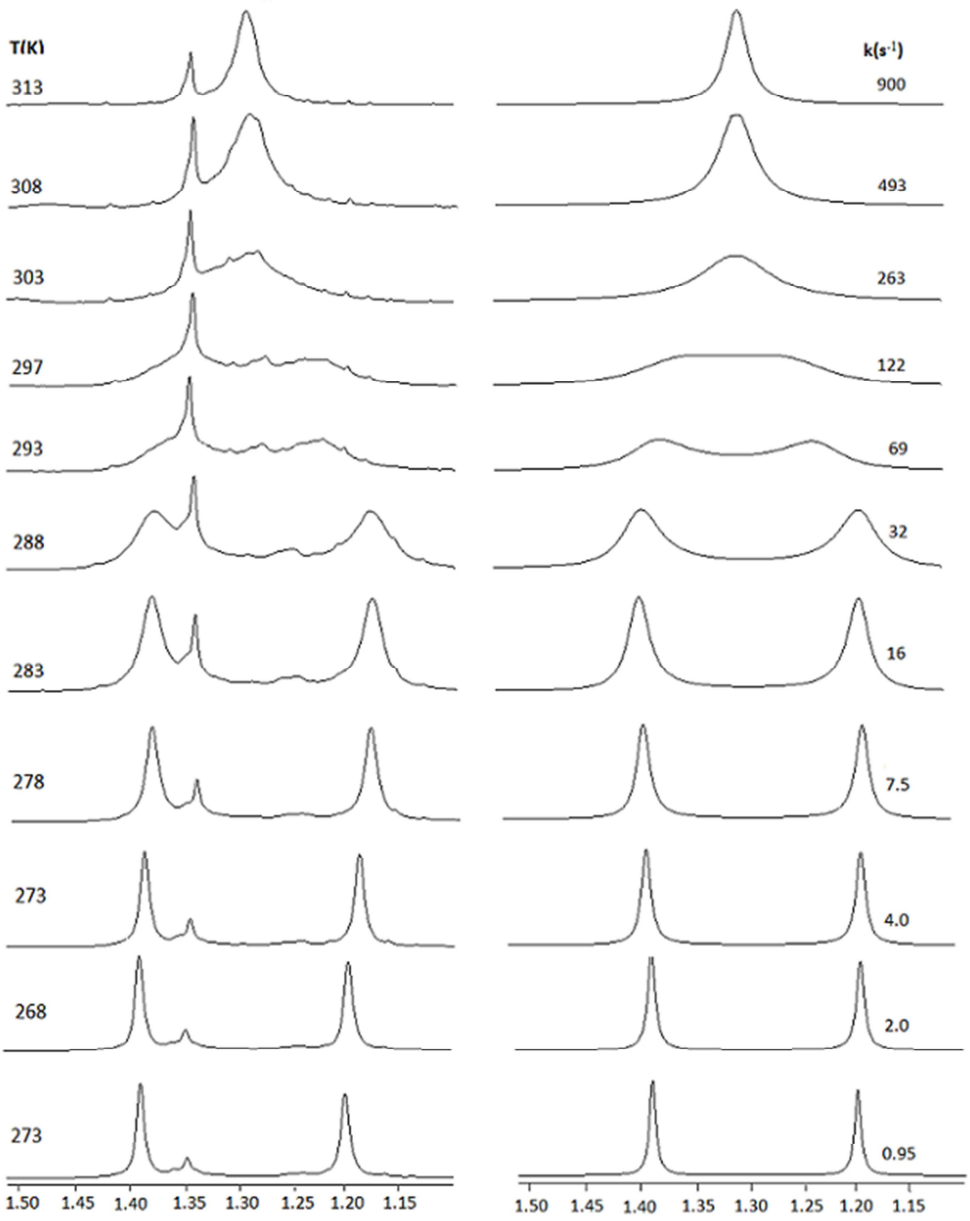


Figure 6. Left: temperature-dependent NMR signals (300 MHz in $CDCl_3$) of the 3,5-di-*t*-butyl protons on the distal phenyl group of compound **21c**. Right: computer simulations using a line shape analysis program (WINDNMR)[40] with the rate constants reported.

We are pleased to see the percent buried volumes calculated for the new complexes **19a** and **21b** are substantially larger. The gold(I) complex **19a** have a calculated $\%V_{Bur}$ of 44.6, almost identical to that of IPrAu(I)Cl. The complex **21b** has a $\%V_{bur}$ of 53.8, which is greater than the very bulky [IPr*Au(I)Cl] complex ($\%V_{bur}$ = 50.4) reported by Nolan.[41] We proceeded to remove the chloride from complexes **19a** and **21b** according to eq. 1 and observed no significant change in their ^{1}H NMR spectra after several days .

The large percent buried volumes for the new gold complexes may be attributed to the o-biphenyl group. The biphenyl substituents through their ortho attachment to the stereogenic carbons place the distal phenyl group inside or near the first coordination sphere centered by the gold atom. Crystal packing forces also contribute to the solid state conformations. The rotational flexibility of the biphenyl axis allows the distal phenyl group to wrap around the Au atom. This analysis is supported by the X-ray structure (although the solution structure may differ from the solid state structure) and by the observation that the rotation around the biphenyl axis is slowed to such a degree that coalescence was observed for complexes **21b** and **21c** at room temperature, rather than at much lower temperatures. Usually mono-substituted biphenyls have free rotation at room temperature on the NMR time scale.[42] However in these complexes the hindrance to free rotation may arise from steric interactions involving the 3,5-dialkyl substituents and the Au-Cl moiety of the complex. The distal phenyl groups are right next to the gold atom and any substituents on the phenyl group could cause steric interactions when rotating around the biphenyl axis.

Table 2. Rate constants for Compounds **21b** and **21c** at Different Temperatures obtained using WINDNMR.[40]

T(K)[a]	k_r (**21b**)	k_r (**21c**)
323	$3.37x10^5$	2606
318	$1.71x10^5$	1678
313	$7.11x10^4$	900
308	5303	493
303	1392	263
297	440	122
293	236	69
288	93	32
283	40	16
278	26	7.5
273	6.3	4.0
268	2.8	2.0
263	1.8	0.95
258	0.41	
253	0.35	

[a] Temperature was not calibrated and was recorded as shown on the instrument dial.

In order to understand the o-biphenyl ligand center C-C bond rotational dynamics in the gold complexes, we performed NMR spectroscopic study for complexes **21b** and **21c** at different temperatures, Figure 4. Variable temperature NMR experiments were performed from –20 to 50 °C with deuterated

chloroform as solvent. At around 5 °C, the rotation around the biphenyl axis becomes slow enough that the signals for the two methyl groups decoalesce, with one at ~2.15 ppm and the other at ~2.4 ppm, Figure 4. At around 30 °C, the rotation around the biphenyl axis becomes fast enough that the signals for the two methyl groups become a single peak centered at ~2.28 ppm, Figure 4.

According to the thermodynamic equation $\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$ and transition state theory,[43] enthalpies, entropies and free energies of activation are related to rate constants by the following equations:

$$k_r = k_B T/h\, e^{\Delta G\ddagger/RT} = (k_B T/h)\, e^{-\Delta H\ddagger/RT}\, e^{\Delta S\ddagger/R} \quad (3)$$

$$\Delta G^{\ddagger} = -RT\ln(k_r h/k_B T) = 1.987 \text{ cal mol}^{-1} \text{ T } (23.76+\ln(T/k_r)) \quad (4)$$

where k_r = rate constant, k_B = Boltzman constant 1.380×10^{-23}, T = Temperature in K, h = Planck's constant 6.626×10^{-34}, R = gas constant 1.987 cal deg^{-1} mol^{-1}, $\ln(h/k_B) = 23.76$.

The free energies of activation ($\Delta G^{\ddagger}$) are calculated from the rate constants (eq. 4 and Table 2), which are obtained from the simulations performed using WINDNMR (see Figure 5 and 6). Plotting the calculated $\Delta G^{\ddagger}$ vs. T, enthalpy and entropy of activation can be estimated, Figure 7 and Table 3.

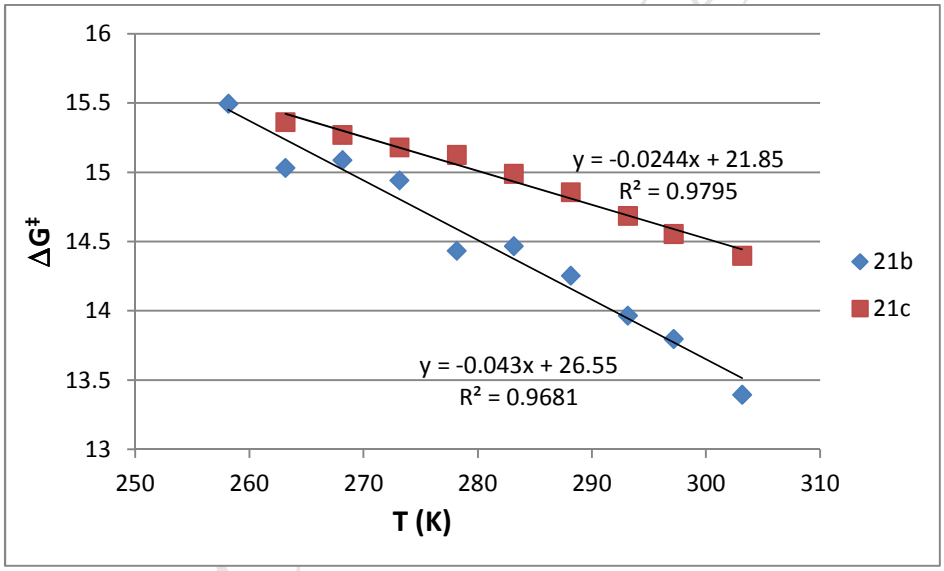


Figure 7. The plot of $\Delta G^{\ddagger}$ vs. T for center C-C bond rotation of the biphenyl substituent of complexes **21b** and **21c**.

The observed biphenyl center C-C bond rotational barriers for the complexes **21b** and **21c** are 14.7 and 13.8 kcal/mol, respectively and the rotational barrier has a significant entropy term. The fact that both complexes have a positive and substantial rotational entropy of activation indicate the biphenyl group experiences more than a simple rotational barrier because simple rotations have small and negative entropy of activation.[44] Our current interpretation for the positive entropy of activation is that the

substituents on the distal phenyl group have restricted movements in the ground state due to steric interactions with the Au-Cl moiety.

Table 3. Activation parameters for center C-C bond rotation of the biphenyl substituent of complexes **21b** and **21c** in $CDCl_3$

Complex[a]	$\Delta G^{\ddagger}$(rotation) (kcal/mol)	$\Delta H^{\ddagger}$(rotation) (kcal/mol)	$\Delta S^{\ddagger}$(rotation) (cal/mol K)	Coalescence Temp (K)
21b	14.0(1)	26.6(0.8)	43.0(3)	293
21c	14.6(1)	21.9(0.4)	24.4(2)	297

[a] The standard errors for the intercept and slope are analyzed with the Excel's LINEST function, which calculates the statistics of the line with least square fit.

In the rotational transition state of the biphenyl group, the substituents on the distal phenyl group may actually have more freedom of movements due to moving away from the Au-Cl. In other words, the methyl (**21b**) and *t*-butyl groups (**21c**) on the distal phenyl may rotate more freely when the biphenyl unit has a twist angle of near zero degree. This explanation is somewhat speculative; however there are literature precedents where external interactions cause the activation entropy to be positive. One literature example similar to this bond rotation dynamics is the report by Bergman and Raymond.[45] They examined the rotational dynamics of encapsulated guest molecules to probe the steric consequences of encapsulation within a host. Encapsulation was found to increase the Ph-CH_2 bond rotational barrier for ortho-substituted benzyl phosphonium guest molecules by 3 to 6 kcal/mol, and also change the entropy of activation from negative to positive. Very similar parallel observations are documented here for the o-biphenyl substituents in the gold(I) complexes. The precursors to gold complexes (imidazoliums **18b** and **18c**) showed no sign of ^{1}H NMR peak broadening at room temperature, which indicates a lower rotational barrier. However once coordinated to Au(I), the rotational barriers are raised so that coalescence is observed for the biphenyl center C-C bond rotation. Therefore the study of the biphenyl rotational barriers support the notion that steric interactions are present between the substituents and the Au-Cl moiety, which in turn, explains the high percent buried volumes calculated for gold complexes **21b** and **21c**.

Conclusion

We have prepared new chiral [(NHC)Au(I)Cl] complexes featuring pairs of o-biphenyl substituents. X-Ray structure analysis was performed for two of the nine gold complexes. Large percent buried volumes are calculated for the two complexes. This indicates the proximity of the ligand substituents to the Au atom. The proximity is further corroborated by a variable temperature NMR study, which showed a free energy activation ~14 kcal/mol for the biphenyl rotational barriers. Normally mono-substituted biphenyls have rotational barriers around 3-10 kcal/mol. The rotational barriers determined for these complexes are greater than usual, which indicates additional steric interactions between substituents and the Au-Cl moiety in addition to the usual biphenyl ortho substituent interactions. Our current efforts include (1) to more precisely substantiate the correlation between steric bulk of the NHC and catalyst

stability by estimating the half-life time of the cationic complexes under given conditions; and (2) to employ the gold complexes as enantioselective catalysts in cycloaddition reactions.

Acknowledgements

Financial support from the NSF (TUES program) and Miami University for the NMR Facility are acknowledged. We are grateful to Professor Hans Reich for assistance with the WINDNMR program. We thank Dr. Ryan Conyers for preparing the [(ADC)Au(I)Cl] complex **23** and Caleb Jones for preparing complex **21a**.

Appendix A. Supporting material

CCDC 1049077-1049078 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Appendix B. Supplementary data

Supplementary material featuring experimental details and NMR spectra related to this article can be found at http://dx.doi.org/.

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High Lights:

- Nine novel chiral [(NHC)Au(I)Cl] complexes are synthesized and characterized.
- X-Ray structure analysis was performed for two of the nine gold complexes. Large percent buried volumes are calculated for the two complexes.
- The new chiral [(NHC)Au(I)Cl] complexes feature pairs of o-biphenyl substituents. The rotational barriers determined for the biphenyl C-C bond rotation in these complexes are greater than usual.

Supporting Information for:

Synthesis and Characterization of Novel Chiral [(NHC)Au(I)Cl] Complexes: Featuring ortho-Biphenyl Substituents

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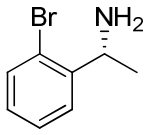
Experimental Procedures and Analytical Data

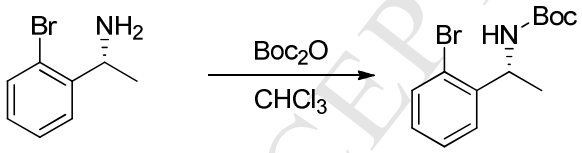
General

Unless otherwise stated, all reactions were carried out under an inert nitrogen atmosphere with anhydrous solvents. Dichloromethane (CH_2Cl_2) was distilled over calcium hydride. Reagents were purchased and used without further purification unless otherwise stated. Yields refer to chromatographically and spectroscopically (^{1}H NMR) homogeneous materials, unless otherwise stated. Reactions were monitored by thin-layer chromatography (TLC) carried out on Merck silica gel plates (60F-254; 0.25 mm) by using UV light as the visualizing agent and an acidic mixture of anisaldehyde, phosphomolybdic acid, ceric ammonium molybdate, or basic aqueous potassium permanganate ($KMnO_4$) and heat as developing agents. Merck silica gel (60, particle size 0.043–0.063 mm) was used for flash column chromatography. NMR spectra were recorded on Bruker Av-500 and Av-300 instruments and calibrated by using residual undeuterated solvent as an internal reference ($CHCl_3$: δ=7.26 (^{1}H), 77.0 ppm (^{13}C)). The following abbreviations (or combinations thereof) were used to explain the multiplicities: s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet, br=broad.



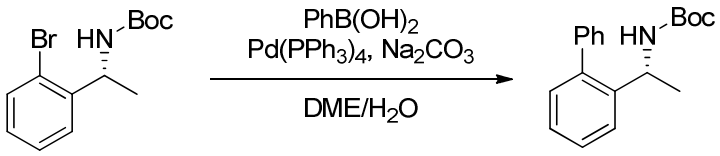
(R)-1-(2-bromophenyl)ethanamine (7).

Using the procedure reported by Klingensmith et. al.[a] The desired amine **7** was produced as a light yellow oil (53%). [α] = –35.3 (0.2, $CHCl_3$) ^{1}H NMR (500 MHz, $CDCl_3$): 1.37-1.38 (d, 1H), 1.57 (bs, 2H), 4.48-4.52 (q, 1H), 7.06-7.1 (t, 1H), 7.26-7.52 (m, 2H), 7.53-7.54 (m, 1H).



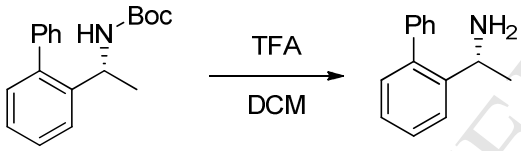
9 (R)-1-(2-Bromo-phenyl)-ethylamine-N-t-Boc.

To a solution of the amine (**7**) (926 mg, 4.65 mmol) in $CHCl_3$ (9 mL) was added Boc anhydride (1.2 mL, 5.12 mmol). The reaction mixture was allowed to stir overnight, concentrated, and purified by column (20% EtOAc/Hex) to yield a white solid (Quant.). [α] = +11.3 (0.02, $CHCl_3$), ^{1}H NMR (500 MHz, $CDCl_3$): 1.26-1.27 (d, 3H), 1.42 (s, 9H), 4.97 (bs, 1H), 5.08 (bs, 1H), 7.08-7.11 (t, 1H), 7.26-7.32 (m, 2H), 7.52-7.53 (d, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): 21.7, 28.3, 50.2, 19.6, 107.6, 110.5, 112.4, 126.4, 127.7, 128.4. LCMS m/z calcd for $C_{13}H_{18}BrNO_2$ 299.0 found 299.2 (M^+).



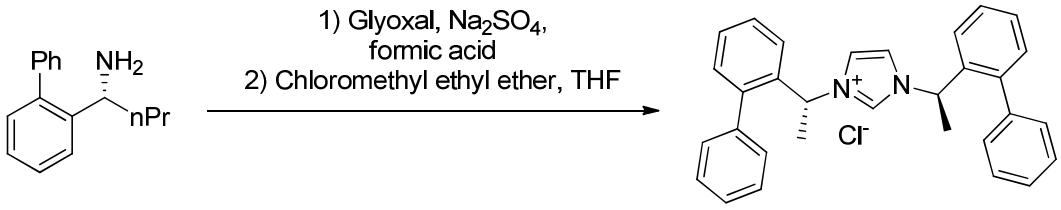
(R) – (+) - 2'- (biphenyl)- α-phenylethyl-N-tert-butylcarbonylamine

A dry, 200 mL RB flask with magnetic stir bar was charged with (R)-1-(2-Bromo-phenyl)-ethylamine-N-t-Boc (**9**) (1.39 g, 4.66 mmol), DME (33 mL), phenylboronic acid (795 mg, 6.52 mmol), Na_2CO_3 (1.48 g, 13.98 mmol), and H_2O (33 mL). The suspension was degassed under N_2 (x3) and then charged with $Pd(PPh_3)_4$ (538 mg, 0.47 mmol), fitted with a reflux condenser, and degassed and additional x2 under N_2. The solution was heated to reflux overnight, cooled to RT, diluted with EtOAc (50 mL), separated, and the aqueous phase was extracted with EtOAc (2x50mL). Combined organics washed with brine, dried over Na_2SO_4, filtered and purified by column (20% EtOAc / Hex) to yield a colorless oil. (73%) [α] = + 33.6 (0.2, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): 1.25-1.26 (d, 3H), 1.39 (bs, 9H), 4.80 (bs, 1H), 4.92 (bs, 1H), 7.18-7.19 (d, 2H), 7.19-7.20 (t, 2H), 7.25-7.34 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): 28.4, 61.2, 124.7, 126.7, 127.1, 127.8, 128.2, 129.3, 130.4, 141.0, 141.9. LCMS m/z calcd for $C_{19}H_{23}NO_2$ 297.2 found 297.4 (M^+).



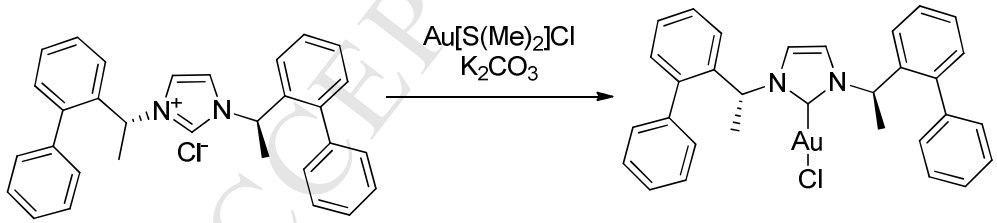
11a (R) – (-) - 2'-(biphenyl)- α-phenylethylamine

To a cooled (0°C) solution of the Boc-protected amine (1.00 g, 3.37 mmol) in $CHCl_3$ (26 mL) was added trifluoroacetic acid (1.81 mL, 23.62 mmol) dropwise. The reaction was allowed to warm to ambient temperature and stirred overnight. The reaction mixture is carefully basified with 10% NaOH (to pH ~ 10) and then separated. The aqueous phase is extracted into EtOAc (3 x 30 mL), combined organics dried over Na_2SO_4, filtered, and solvent removed under reduced pressure to provide the free amine as a light yellow oil (92%). [α] = -23.6 (0.01, $CHCl_3$) ^{1}H NMR (500 MHz, $CDCl_3$): 1.31-1.33 (d, 3H), 3.53 (bs, 2H), 4.24-4.28 (q, 1H), 7.18-7.20 (d, 1H), 7.25-7.29 (m, 2H), 7.35-7.41 (m, 3H), 7.58-7.60 (d, 1H) ^{13}C NMR (125 MHz, $CDCl_3$): 25.3, 46.7, 125.2, 126.4, 126.9, 127.9, 128.1, 129.3, 130.1, 140.7, 141.4, 145.0 LCMS m/z calcd for $C_{14}H_{15}N$ 197.1, found 196.1 (M^+-H^+).



16a 1,3-bis((R)-1-([1,1'-biphenyl]-2-yl)ethyl)-1H-imidazol-3-ium chloride

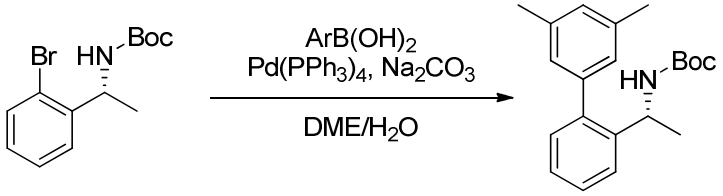
In a dry RB flask under N_2, A solution of 40% wt glyoxal (0.17 mL, 1.48 mmol) in DCM (3.0 mL) was charged with oven dried Na_2SO_4 (839 mg, 5.91 mmol), then formic acid (0.005 mL, 0.118 mmol). To this suspension was added a solution of the corresponding amine (588 mg, 2.95 mmol) in DCM (3.0 mL), allowed to stir for 30 minutes, then another portion of Na_2SO_4 (839 mg, 5.91 mmol) was added, and allowed to stir for 3 hours. The solution was filtered, solvent removed, and used in the next step without further purification. In a dry RB flask under N_2, to a solution of chlormethyl ethyl ether (0.14 mL, 1.48 mmol) in THF (1.0 mL) is added 1 drop of water (approx. 0.01 mL), then a solution of the diimine (615 mg, 1.48 mmol) in THF (2.0 mL). The mixture is fitted with a reflux condenser and stirred at RT for 24 h, then heated to 45^{o}C for 16h. The reaction mixture was cooled to RT, quenched with H_2O (10 mL), separated, and aqueous portion extracted into DCM (3 x 10 mL). Combined organics dried over Na_2SO_4, filtered solvent removed and purified by column (5% MeOH/DCM) to yield a brown solid. (63%) [α] = +61.6 (0.01, $CHCl_3$) ^{1}H NMR (500 MHz, $CDCl_3$): 1.91-1.93 (d, 6H), 5.82-5.83 (q 2H), 6.57 (s, 2H), 7.14-7.49 (m, 14H), 9.71 (s, 1H) ^{13}C NMR (125 MHz, $CDCl_3$): 21.1, 50.8, 56.7, 120.2, 126.4, 128.0, 128.5, 128.7, 128.9, 129.2, 130.8, 135.1, 136.5, 139.4, 142.0. LCMS m/z calcd for $C_{31}H_{29}N_2Cl$ 464.2 found 428.6 (M^+-Cl^-)



19a (1,3-bis((R)-1-([1,1'-biphenyl]-2-yl)ethyl)-2,3-dihydro-1H-imidazol-2-yl)gold(I) chloride

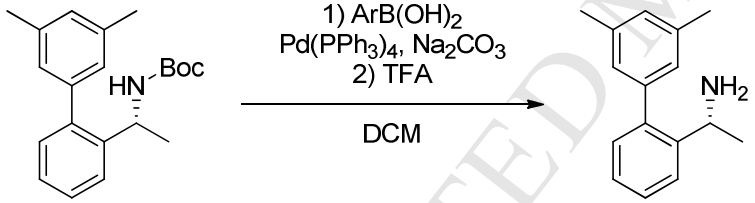
In a dry 10 mL RB flask under N_2, the imidazolium chloride (**16a**) (90 mg, 0.19 mmol), Au[$S(Me)_2$]Cl (57.1 mg, 0.19 mmol), and K_2CO_3 (27 mg, 0.19 mmol) were suspended in acetone (1.0 mL). The flask was fitted with a reflux condenser, and the reaction was heated to reflux for 3h. The reaction was cooled, solvent removed under reduced pressure, residue re-suspended in DCM then filtered through a pad of celite and silica. Compound purified by column chromatography (50% EtOAc/Hex) to yield a white solid

(28%). [α] = -34.3 (0.01, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): 1.62-1.64 (d, 6H), 5.95-5.99 (q, 2H), 6.34 (s, 2H), 7.01-7.02 (d, 3H), 7.01-7.02 (d, 2H), 7.29-7.46 (m, 9H) ^{13}C NMR (125 MHz, $CDCl_3$): 21.6, 56.9, 117.3, 125.9, 127.6, 127.7, 128.3, 128.5, 128.9, 130.9, 136.2, 139.7, 143.1, 171.6.



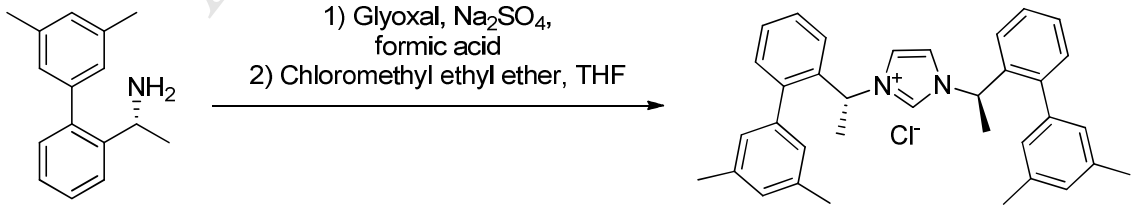
tert-butyl (1-(3',5'-dimethyl-[1,1'-biphenyl]-2-yl)ethyl)carbamate:

Using the same general procedure as reported for (R) – (-) - 2'- (biphenyl)-α-phenylethyl-N-tert-butylcarbonylamine**,** the carbamate was obtained as a white foam, (92%). [α] =+16.7 ^{1}H NMR (500 MHz, $CDCl_3$): 1.28 (s, 3H), 1.42 (s, 9H), 2.37 (s, 6H), 4.78 (bs, 1H), 4.92 (bs, 1H), 6.98-7.00 (d, 3H), 7.19-7.21 (d, 1H), 7.26-7.29 (t, 1H), 7.33-7.36 (t, 1H), 7.41-7.42 (d, 1H) ^{13}C NMR(125 MHz, $CDCl_3$): 21.4, 28.4, 47.4, 79.0, 124.9, 126.8, 127.1, 127.6, 128.7,130.5, 137.6, 140.8, 141.2, 141.5, 154.5. LCMS m/z calcd for $C_{21}H_{27}NO_2$ 325.4 found 348.2 (M+Na)



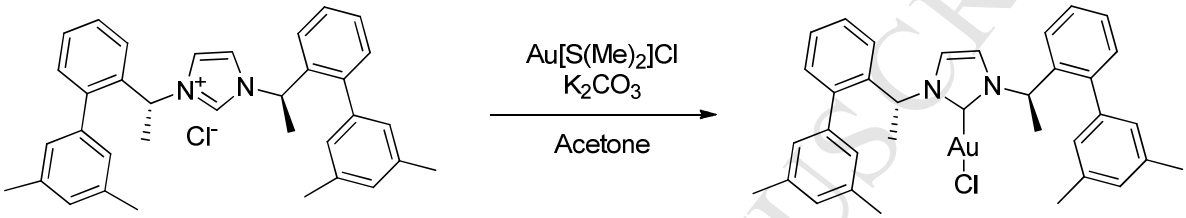
11b (R)-1-(3',5'-dimethyl-[1,1'-biphenyl]-2-yl)ethanamine

Same procedure as reported for **11a**, obtained as a yellow oil (Quant.) [α] = -19.5 (0.1, $CHCl_3$) ^{1}H NMR (500 MHz, $CDCl_3$): 1.29-1.31 (d, 3H), 1.47 (bs, 2H), 2.36 (s, 6H), 4.22-4.26 (q, 1H), 6.91 (s, 2H), 7.00 (s, 1H), 7.16-7.17 (d, 1H), 7.23-7.26 (t, 1H), 7.36-7.39 (t, 1H), 7.58-7.59 (d, 1H) ^{13}C NMR (125 MHz, $CDCl_3$): 21.4, 25.3, 46.7, 125.0, 126.2, 127.1, 127.8, 128.6, 129.9, 137.6, 140.9, 141.3, 145.1. LCMS m/z calcd for $C_{16}H_{19}N$ 225.3 found 224.3 ($M-H^+$)



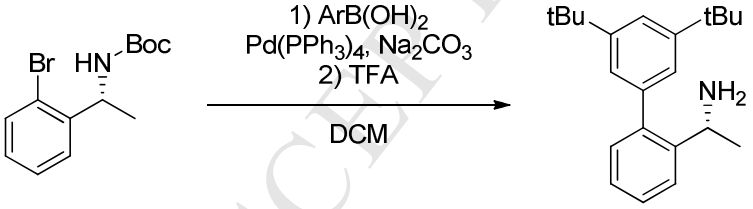
16b 3-((R)-1-(3',5'-dimethyl-[1,1'-biphenyl]-2-yl)ethyl)-1-((S)-1-(3',5'-dimethyl-[1,1'-biphenyl]-2-yl)ethyl)-1H-imidazol-3-ium chloride

Following the same general procedure for **16a**, **16b** was produced as a brown solid (17%) [α] = +89.4 (0.02, $CHCl_3$) ^{1}H NMR (500 MHz, $CDCl_3$): 2.11-2.12 (d, 2H), 2.34 (s, 12H), 5.75-5.78 (q, 2H), 6.57 (s, 2H), 6.78 (bs, 5H), 7.00 (s, 2H), 7.23-7.24 (d,3H), 7.36-7.44 (m, 4H), 7.54-7.55 (d, 2H), 10.45 (s, 1H) ^{13}C NMR (125 MHz, $CDCl_3$):: 21.4, 21.7, 23.5, 57.1, 120.5, 136.5, 136.6, 128.7, 128.9, 129.6, 130.6, 135.5, 136.5, 138.5, 139.5, 141.9. LCMS m/z calcd for $C_{35}H_{37}N_2Cl$ 520.3 found 485.7 ($M\text{-}Cl^+$)



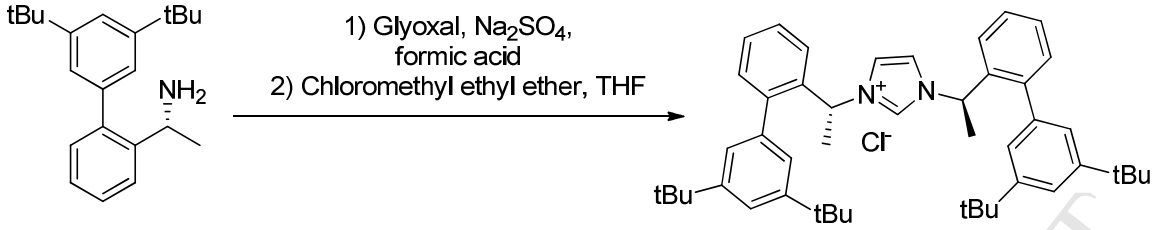
19b (1,3-bis((R)-1-(3',5'-dimethyl-[1,1'-biphenyl]-2-yl)ethyl)-2,3-dihydro-1H-imidazol-2-yl)gold(I) chloride:

Following the same general procedure for **19a, 19 b** was obtained as a light yellow solid (41%) [α] = +15.4 (0.05, $CHCl_3$). ^{1}H NMR(500 MHz, $CDCl_3$): 1.60-1.61 (d, 6H), 2.34 (s, 12H), 6.06-6.10 (q, 2H), 6.30 (s, 2H), 6.63 (bs, 4H), 6.94 (s, 2H), 7.19-7.20 (d, 2H), 7.37-7.42 (m, 8H). ^{13}C NMR (125 MHz, $CDCl_3$): 21.5, 21.6, 56.8, 117.1, 125.9, 126.2, 127.5, 128.5, 129.3, 130.9, 135.9, 138.1, 139.6, 143.5, 171.6.



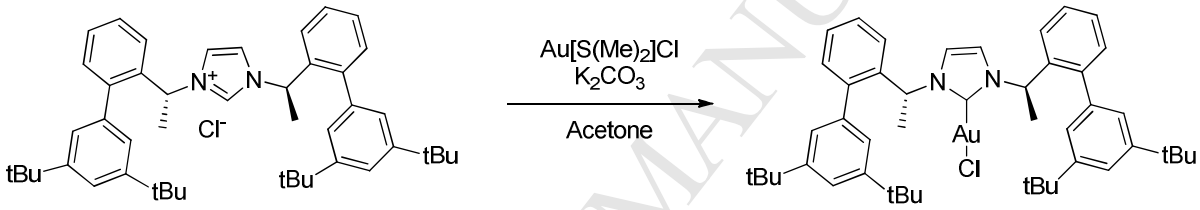
11c (R)-tert-butyl (1-(3',5'-di-tert-butyl-[1,1'-biphenyl]-2-yl)ethyl)carbamate:

Following the same general procedure for **11a**, **11c** was obtained as a yellow oil (Quant.). [α] = +30.2 (0.1, $CHCl_3$) ^{1}H NMR (500 MHz, $CDCl_3$): 1.35 (s, 21H), 1.52 (bs, 2H), 4.19-4.23 (q, 1H), 7.14 (s, 2H), 7.24-7.29 (m, 2H), 7.38-7.41 (t, 2H), 7.60-7.62 (d, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): 25.5, 31.5, 34.9, 46.8, 120.7, 123.6, 125.2, 126.3, 127.7, 130.1, 140.4, 141.7, 145.4, 150.3. LCMS m/z calcd for $C_{27}H_{39}NO_2$ 409.3 found 409.1 (M^+)



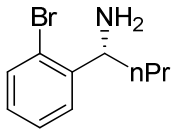
16c 1,3-bis((R)-1-(3',5'-di-tert-butyl-[1,1'-biphenyl]-2-yl)ethyl)-1H-imidazol-3-ium chloride:

Following the general procedure for **16a, 16c** was obtained as a brown solid (42%). [α] = +54.1 (0.1, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): 1.31 (s 36H), 2.32-2.34 (d, 6H), 5.46-5.50 (q, 2H), 6.40 (s, 2H), 7.01 (s, 4H), 7.27-7.29 (d, 2H), 7.35-7.38 (t, 2H), 7.42-7.45 (t, 2H), 7.74-7.76 (d, 2H), 11.19 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): 31.5, 31.6, 34.9, 57.9, 120.9, 121.8, 123.1, 127.1, 128.7, 129.0, 130.2, 136.2, 138.9, 142.4, 151.3. LCMS m/z calcd for $C_{47}H_{61}N_2Cl$ 688.4 found 654.0 (M^+-Cl^-)



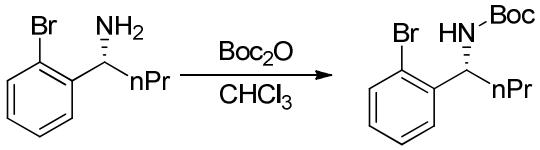
19c (1,3-bis((R)-1-(3',5'-di-tert-butyl-[1,1'-biphenyl]-2-yl)ethyl)-2,3-dihydro-1H-imidazol-2-yl)gold(I) chloride:

Same procedure as reported for **19a**, white solid (72%) [α] = +49.0 (0.02, $CHCl_3$) ^{1}H NMR (500 MHz, $CDCl_3$): 1.31 (s, 36H), 1.70-1.71 (d, 6H), 5.86-5.91 (q, 2H), 6.64 (s, 2H), 6.99 (s, 4H), 7.18-7.25 (m, 2H), 7.27-7.29 (m, 2H), 7.36-7.39 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): 22.4, 31.6, 34.9, 57.6, 117.8, 121.6, 122.9, 126.0, 127.6, 128.3, 1313.2, 136.9, 139.1, 143.5, 150.8, 172.0.



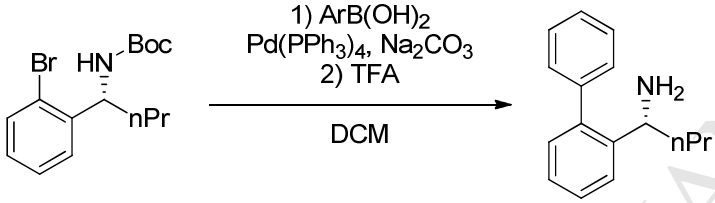
8 (R)-1-(2-bromophenyl)butan-1-amine:

Using the procedure reported by Dalmolen et. al.[b], the starting amine was produced as a light yellow oil. (65%) [α] = +17.6 (0.1, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): 0.87-0.93 (t, 3H), 1.29-1.31 (m, 1H), 1.41-4.43 (m, 1H), 1.84-7.89 (m, 2H), 4.60-4.63 (t, 1H), 7.12-7.14 (t, 1H), 7.42-7.44 (d, 1H), 7.54-7.56 (d, 1H), 7.61-7.62 (d, 1H).



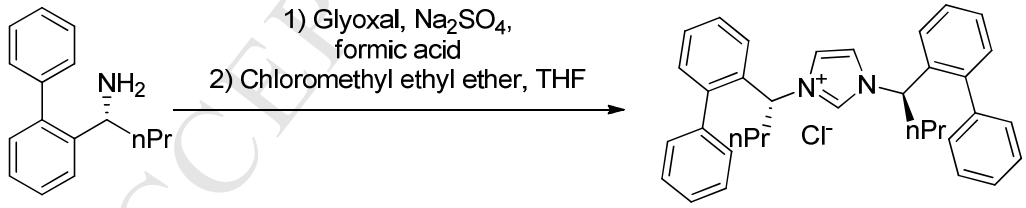
10 (R)-tert-butyl (1-(2-bromophenyl)butyl)carbamate:

Following the general procedure for **9**, the boc protected amine **10** was obtained in 98% yield as a white foam. [α] = +0.4 (0.1, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): 0.89-0.95 (t, 3H), 1.27-1.49 (m, 13H), 1.53 (bs, 1H), 1.75 (bs, 1H), 4.98 (bs, 2H), 7.07-7.10 (t, 1H), 7.23-7.32 (m, 2H), 7.51-7.53 (d, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): 13.7, 13.8, 27.4, 28.4, 38.2, 15.3, 85.2, 122.9, 126.3, 127.1, 127.6, 128.3, 128.5, 133.2, 155.1. . LCMS m/z calcd for $C_{15}H_{22}NO_2$ 327.1 found 327.5 (M^+)



12a (R)-1-([1,1'-biphenyl]-2-yl)butan-1-amine

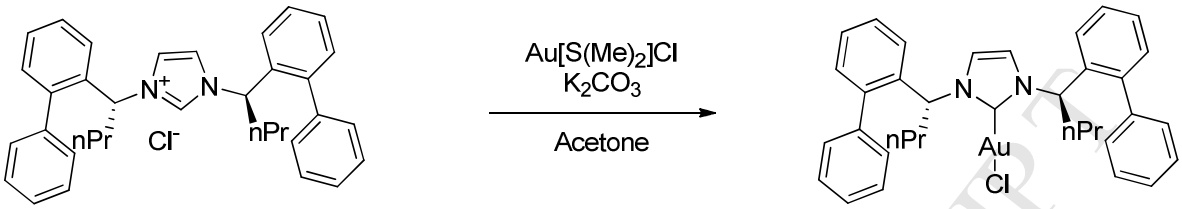
Using the same general procedure as reported for **11a**, **12a** was isolated as a yellow oil. (63%). [α] (0.02 $CHCl_3$) = +18.7. ^{1}H NMR (500 MHz, $CDCl_3$): 0.67-0.70 (t, 3H), 1.03-1.05 (m, 1H), 1.13-1.14 (m, 1H), 1.35 (bs, 1H), 1.49-1.55 (m, 2H), 3.93-3.96 (t, 1H), 7.11-7.13 (dd, 1H), 7.17-7.19 (m, 3H), 7.21-7.35 (m, 4H), 7.46-7.48 (dd, 1H). LCMS m/z calcd for $C_{16}H_{19}N$ 225.2 found 223.9 (M^+-H^+)



17a 1,3-bis((R)-1-([1,1'-biphenyl]-2-yl)butyl)-1H-imidazol-3-ium chloride:

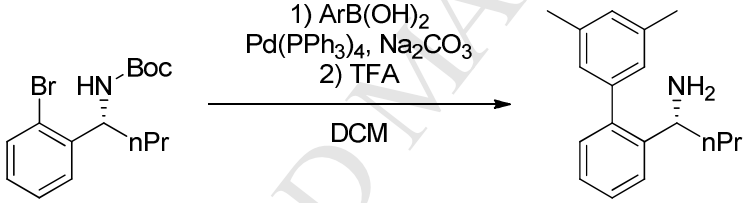
Using the general procedure for **16a**, **17a** was was obtained as a light brown foam (37%) [α] = +42.8. ^{1}H NMR (500 MHz, $CDCl_3$): 0.88 (t, 6H), 1.16-1.30 (m, 4H), 2.44-2.49 (m, 2H), 2.56-2.60 (m, 2H), 5.45-5.48 (t, 2H), 6.76 (s, 2H), 7.1-7.11 (d, 2H), 7.24-7.25 (dd, 3H), 7.29-7.52 (m, 8H), 7.52-7.55 (t, 2H), 7.90-7.91 (d, 2H), 10.28 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): 13.5, 19.5, 36.3, 61.3, 120.7, 127.2, 127.3,

127.9, 128.3, 128.4, 128.8, 128.9, 129.2, 129.5, 130.5, 134.3, 136.1, 139.8, 142.3. . LCMS m/z calcd for $C_{35}H_{37}N_2Cl$ 520.3 found 485.7 (M^+-Cl^-).



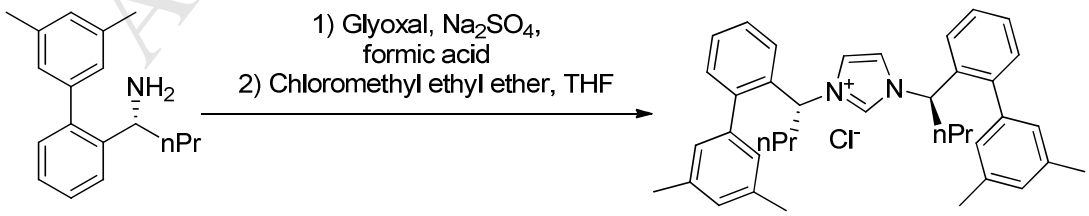
20a (1,3-bis((R)-1-([1,1'-biphenyl]-2-yl)butyl)-2,3-dihydro-1H-imidazol-2-yl)gold(I) chloride:

Using the general procedure reported for **19a**, **20a** was isolated as a white solid (80%), [α]= +13.8 (0.3, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): 0.83-0.85 (t, 6H), 1.13-1.19 (m, 1.19), 1.22-1.30 (m, 2H), 1.98-2.06 (m, 4H), 5.90-5.94 (t, 2H), 6.63 (s, 2H), 7.14-7.16 (d, 4H), 7.23-7.25 (d, 2H), 7.37-7.45 (m, 12H). ^{13}C NMR (125 MHz, $CDCl_3$): 13.5, 19.6, 37.3, 61.0, 118.11, 125.9, 127.7, 127.8, 128.22, 128.7, 128.9, 131.0, 135.9, 139.8, 143.2, 171.9.



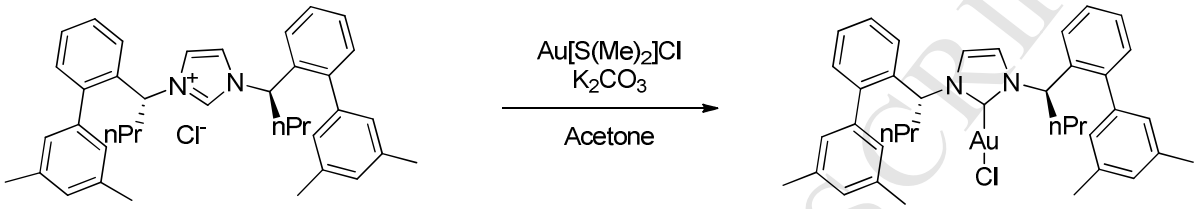
12b (R)-1-(3',5'-dimethyl-[1,1'-biphenyl]-2-yl)butan-1-amine:

Using the general procedure reported for **11a**, **12b** was obtained as a light yellow oil (89%). [α] = +2.1 (0.3, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): 0.74-0.79 (t, 3H), 1.12-1.36 (m, 1H), 1.15-1.16 (m, 1H), 1.51-1.65 (m, 2H), 2.35 (s, 6H), 4.01-4.04 (t, 1H), 6.89 (s, 2H), 6.99 (s, 1H), 7.16-7.18 (d, 1H), 7.22-7.27 (m, 2H), 7.35-7.38 (t, 2H), 7.51-7.57 (d, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): 13.9, 19.8, 21.4, 41.5, 50.7, 125.5, 126.2, 126.8, 127.2, 127.7, 128.3, 128.5, 128.7, 129.9, 137.5, 141.4, 141.4,144.2. . LCMS m/z calcd for $C_{18}H_{23}N$ 253.2 found 254.6 (M^++H^+).



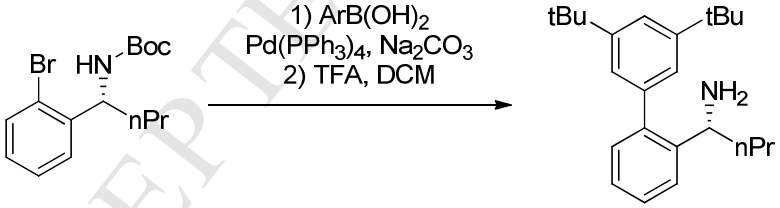
17b 1,3-bis((R)-1-(3',5'-dimethyl-[1,1'-biphenyl]-2-yl)butyl)-1H-imidazol-3-ium chloride:

Following the general procedure for **16a, 17b** was obtained as a light brown solid. (42%). [α] = +61.9 ^{1}H NMR (500 MHz, $CDCl_3$): 0.86-0.89 (t, 6H), 1.93-1.23 (m, 4H), 2.28 (s, 12H), 5.43-5.46 (t, 2H), 6.71 (s, 4H), 6.96 (s, 3H), 7.18-7.19 (d, 2H), 7.25-7.27 (d, 2H), 7.33-7.36 (t, 2H), 7.45-7.48 (t, 2H), 7.86-7.87 (d, 2H), 10.48 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$):13.5, 13.6, 19.5, 21.2, 21.4, 23.4, 53.5, 61.3, 120.7, 126.7, 127.1, 128.8, 18.9, 129.0, 129.5, 129.9, 130.4, 134.2, 135.9, 137.9, 138.3, 139.7, 142.4. . LCMS m/z calcd for $C_{39}H_{45}N_2Cl$ 576.3 found 541.7(M^+-Cl^-).



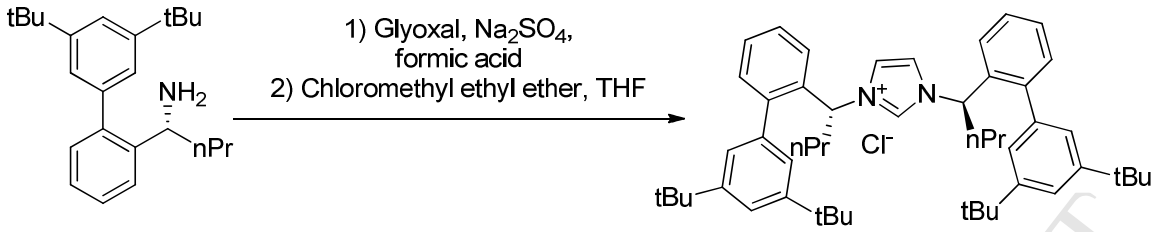
20b (1,3-bis((R)-1-(3',5'-dimethyl-[1,1'-biphenyl]-2-yl)butyl)-2,3-dihydro-1H-imidazol-2-yl)gold(I) chloride:

Following the same general procedure for **19a, 20b** was isolated as a light yellow solid (47%). [α]= +21.6 (0.06, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): 0.81-0.84 (t, 6H), 1.12-1.17 (m, 2H), 1.21-1.25 (m, 2H), 1.96-2.02 (m ,4H), 2.33 (s, 12H), 5.92-5.95 (t, 2H), 6.58 (s, 2H), 6.71 (bs, 4H), 6.98 (s, 2H), 7.21-7.22 (d, 2H), 7.33-7.36 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$): 13.6, 19.7, 21.5, 37.5, 61.1, 117.8, 126.1, 126.5, 127.4, 128.2, 129.6, 131.1, 135.4, 138.2, 139.6, 143.7, 171.7.



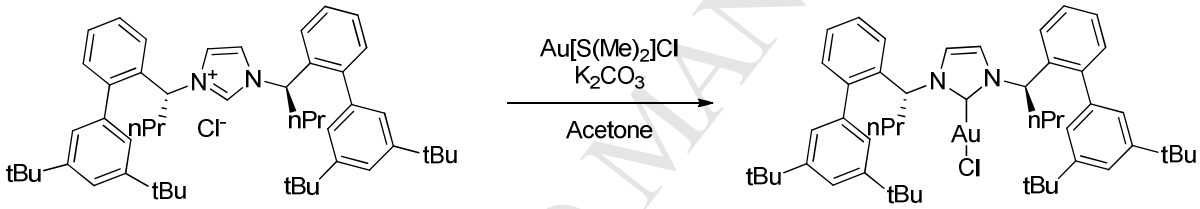
12c (R)-1-(3',5'-di-tert-butyl-[1,1'-biphenyl]-2-yl)butan-1-amine:

Following the same general procedure as reported for **11a, 12c** was obtained as an orange oil (Quant.) [α] = -13.2 (0.1, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): 0.74-0.77 (t, 3H), 1.12-1.14 (m, 1H), 1.15-1.35 (m, 1H), 1.46 (s, 18H), 1.48 (bs, 2H), 1.56-1.65 (m, 2H), 3.97-4.00 (t, 1H), 7.11 (s, 2H), 7.12-7.28 (m, 2H), 7.36-7.40 (m, 2H), 7.53-7.56 (d, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): 13.9, 19.9, 31.5, 34.9, 41.6, 51.0, 120.6, 123.7, 125.5, 126.1, 127.6, 129.9, 140.5, 142.3, 144.6, 150.3. . LCMS m/z calcd for $C_{24}H_{35}N$ 337.3 found 360.5 (M^++Na^+).



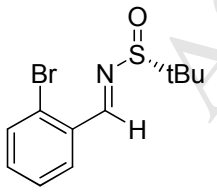
17c 1,3-bis((R)-1-(3',5'-di-tert-butyl-[1,1'-biphenyl]-2-yl)butyl)-1H-imidazol-3-ium chloride:

Following the same general procedure as reported for **16a, 17c** was obtained as a brown foam (68%). [α] = +88.6 (0.03, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): 0.93-0.94 (t, 6H), 1.18-1.24 (m, 4H), 1.33 (s, 36H), 2.69-2.78 (m, 2H), 2.88-2.94 (m, 2H), 5.24-5.27 (t, 2H), 6.42 (s, 2H), 6.99 (bs, 4H), 7.25-7.28 (m, 4H), 7.35-7.38 (m, 2H), 7.47 (s, 1H), 7.52-7.54 (t, 2H), 8.11-8.13 (d, 2H), 11.35 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): 13.5, 19.7, 31.4, 31.5, 34.9, 36.0, 62.1, 120.6, 120.8, 131.6, 123.5, 127.4, 128.6, 129.4, 129.9, 135.1, 139.3, 142.9. . LCMS m/z calcd for $C_{51}H_{69}N_2Cl$ 709.5 found 710.1 (M^+-Cl^-).



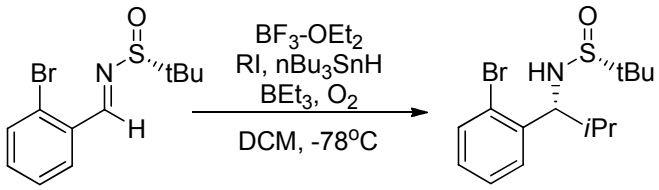
20c (1,3-bis((R)-1-(3',5'-di-tert-butyl-[1,1'-biphenyl]-2-yl)butyl)-2,3-dihydro-1H-imidazol-2-yl)gold(I) chloride:

Following the same general procedure as reported for **19a, 20c** was isolated as a light yellow solid (77%). [α] = +38.1 (0.02, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): 0.72-0.75 (t, 6H), 1.05-1.16 (m, 4H), 1.32 (s, 36H), 1.99-2.09 (m, 2H), 2.22-2.29 (m, 2H), 5.78-5.81 (t, 2H), 6.57 (s, 2H), 7.01 (s, 4H), 7.25-7.31 (m, 4H), 7.35-7.36 (d, 4H), 7.43 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): 13.4, 19.6, 31.6, 31.7, 34.9, 37.6, 61.9, 118.4, 121.6, 123.1, 126.3, 127.5, 128.1, 131.0, 136.1, 139.3, 143.9, 150.9, 171.6.



13 (R,E)-N-(2-bromobenzylidene)-2-methylpropane-2-sulfinamide:

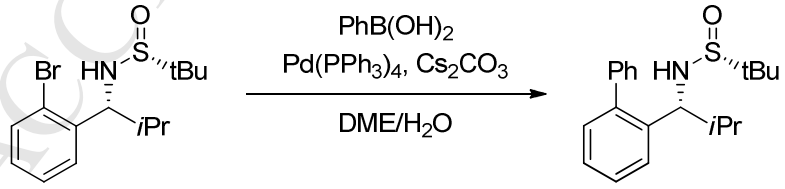
Synthesized according to the procedure reported by Fernandez-Sals et. al.[c] obtained as a yellow oil (94%). ^{1}H NMR (500 MHz, $CDCl_3$): 1.28 (s, 9H), 7.42-7.47 (m, 2H), 7.52-7.54 (d, 1H), 8.12-8.14 (d, 1H), 8.64 (s, 1H).



14 (R)-N-((R)-1-(2-bromophenyl)-2-methylpropyl)-2-methylpropane-2-sulfinamide:

In a dry 250 mL flask under N_2, the (R)-(-) sulfonylaldimine **13** (700 mg, 2.46 mmol) was dissolved in DCM (62 mL) and charged with BF_3-OEt_2 (0.6 mL, 5.17 mmol), stirred for 5 minutes, then cooled to -78^o C in an acetone /dry ice bath. The 2-iodopropane (2.5 mL, 24.64 mmol), tributyltin hydride (1.7 mL, 6.16 mmol), triethylborane (1M in hexanes) (6.2 mL, 6.16 mmol) were added in order. The volume of oxygen (25 mL/mmol) was added via syringe, bubbling through the solution. After 1 hour, the reaction is quenched with sat aq. $NaHCO_3$ (50 mL). The suspension is filtered over celite, separated, and the aqueous portion is extracted into DCM (3x50 mL). Combined organics washed with brine, dried over Na_2SO_4, filtered, and solvent removed. The resulting oil was treated with petroleum ether until crystals begin to form then cooled in an ice bath. The resulting solid was collected by filtration and rinsed thoroughly with petroleum ether to yield white needles (52%). [α] = -57.5. (0.3, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): 0.86-0.88 (d, 3H), 0.99-1.00 (d, 3H), 1.21 (s, 9H), 2.18-2.21 (m, 1H), 3.74 (bs, 1H), 4.47 (bs, 1H), 7.09-7.12 (t, 1H), 7.26-7.32 (m, 2H), 7.53-7.54 (d, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): 19.8, 22.6, 33.7, 56.5, 127.5, 128.8, 129.0, 133.3, 141.2. . LCMS m/z calcd for $C_{24}H_{22}BrNOS$ 331.1 found 330.3 (M^+-H^+).

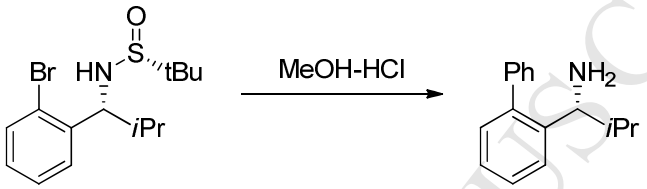
General procedure Suzuki Coupling sulfonamide of **14**:



N-(1-([1,1'-biphenyl]-2-yl)-2-methylpropyl)-2-methylpropane-2-sulfinamide:

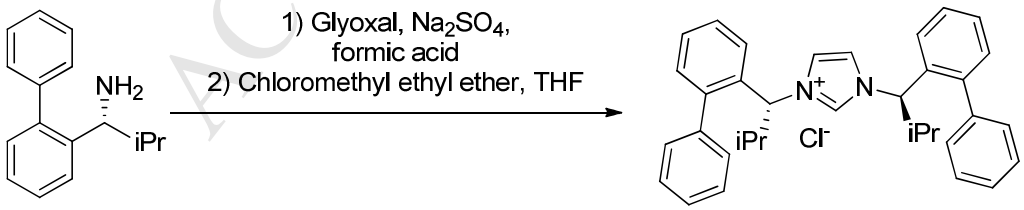
A dry 25 mL RB flask under N_2 was charged with the sulfonamide (**14**) (100 mg, 0.301 mmol), Cs_2CO_3 (294.2 mg, 0.903 mmol), and the boronic acid (63.1 mg, 0.421 mmol). The flask is purged and back-filled with N_2, then a 1:1 solution of DME:H_2O (4.3 mL) was added via syringe. The stirred suspension was

degassed with N_2 (x3) , then charged with $Pd(PPh_3)_4$ (34.7 mg, 0.030 mmol). The reaction flask was fitted with a reflux condenser and then degassed with N_2 again. The reaction was heated to reflux overnight, cooled to RT, diluted with 10 mL H_2O, and extracted into DCM (3X10mL). Combined organics washed with brine, dried over Na_2SO_4, filtered, and purified by column (30% EtOAc:Hex). $[\alpha]$ = -165.4 (0.02 $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): 0.64-0.66 (d, 2H), 0.87-0.88 (d,2H), 1.23 (s, 9H), 1.90-1.97 (m, 1H), 3.51-3.52 (d, 1H), 4.18-4.21 (t, 1H), 7.21 -7.23 (d, 1H), 7.287-7.295 (t, 1H), 7.37-7.39 (m, 7H). ^{13}C NMR (125 MHz, $CDCl_3$): 19.5, 19.6, 22.7, 36.5, 15.2, 62.5, 126.3, 126.7, 127.0, 127.8, 128.1, 129.8, 130.4, 140.1, 141.3, 141.8. . LCMS m/z calcd for $C_{20}H_{27}NOS$ 329.2 found 327.9 (M^+-H^+).



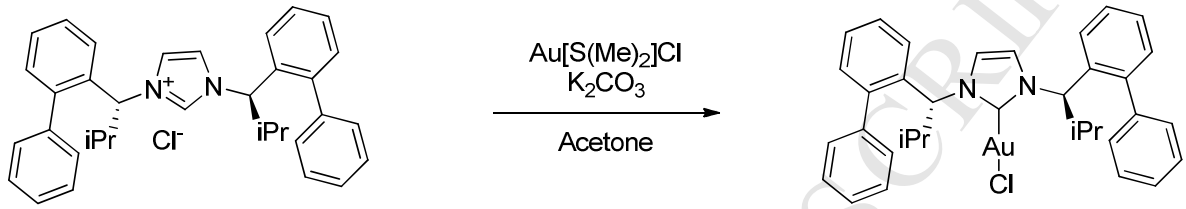
15a (R)-1-([1,1'-biphenyl]-2-yl)-2-methylpropan-1-amine:

In a dry 10 mL rb flask under N_2, methanol (0.5 mL) was cooled to 0^{o}C, then Acetyl Chloride (0.04 mL, 0.526 mmol) was added to generate the acidic methanol solution. The acidic methanol solution was warmed to RT, then added to N-(1-([1,1'-biphenyl]-2-yl)-2-methylpropyl)-2-methylpropane-2-sulfinamide in another dry flask under N_2 via syringe. The solution was stirred for 2 hours, then basified with 10% wt. aq. NaOH, extracted into DCM (3 X 10 mL). Combined organics washed with brine, dried over Na_2SO_4, filtered and solvent removed, purified by column (10% MeOH:DCM) to yield product as a light yellow oil. (83%). $[\alpha]$ = -33.5 (0.01, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): 0.60-0.61 (d, 3H), 0.94-0.95 (d, 3H), 1.66 (bs, 2H), 1.83-1.89 (m, 1H), 3.67-3.70 (d, 1H), 7.20-7.21 (d, 1H), 7.22-7.28 (m, 3H), 7.29-7.40 (m, 4H), 7.41-7.42 (d, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): 14.2, 29.2, 35.4, 27.5, 126.0, 126.2, 126.8, 127.8, 128.0, 129.4, 129.9, 141.7, 141.8, 143.2. . LCMS m/z calcd for $C_{16}H_{19}N$ 225.2 found 224.3 (M^+-H^+).



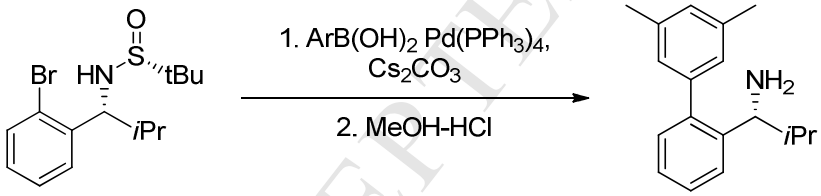
18a 1,3-bis((R)-1-([1,1'-biphenyl]-2-yl)-2-methylpropyl)-1H-imidazol-3-ium chloride:

Following the general procedure for **16a**, **18a** was obtained as a light brown, glassy solid (62%). [α] = -60.4 (0.01, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): 0.68-0.69 (d, 6H), 0.86-0.87 (d, 6H), 3.21-3.26 (m, 2H), 4.83-4.85 (d, 2H), 6.85 (s, 2H), 7.00 (bs, 4H), 7.10-7.14 (d, 2H), 7.29-7.34 (m, 10H), 7.49-7.52 (m, 2H), 10.01 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): 19.8, 20.1, 31.5, 53.4, 38.3, 121.2, 127.2, 127.9, 128.7, 128.8, 128.9, 129.4, 130.3, 134.2, 134.3, 137.8, 142.6. LCMS m/z calcd for $C_{35}H_{37}N_2Cl$ 520.3 found 485.6 (M^+-Cl^-).



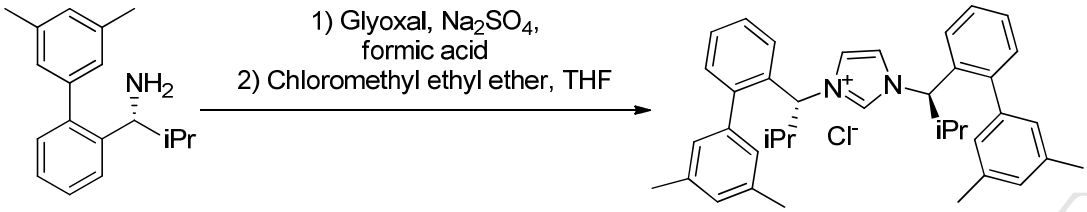
21a (1,3-bis((R)-1-([1,1'-biphenyl]-2-yl)-2-methylpropyl)-2,3-dihydro-1H-imidazol-2-yl)gold(I) chloride:

Following the general procedure for **19a**, **21a** was isolated as a white foam (43%). [α] = +100.0 (0.02, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): 0.77-0.78 (d, 6H), 0.97-0.98 (d, 6H), 2.70-2.76 (m, 2H), 5.46-5.48 (d, 2H), 6.48 (s, 2H), 6.98 (bs, 4H), 7.22-7.23 (d, 2H), 7.24-7.41 (m, 8H), 7.47-7.48 (t, 2H), 7.78-7.81 (d, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): 14.2, 20.4, 20.6, 21.1, 31.9, 60.4, 67.3, 118.5, 126.9, 127.8, 128.2, 128.3, 128.8, 129.1, 131.1, 134.8, 139.7, 144.4, 170.1.



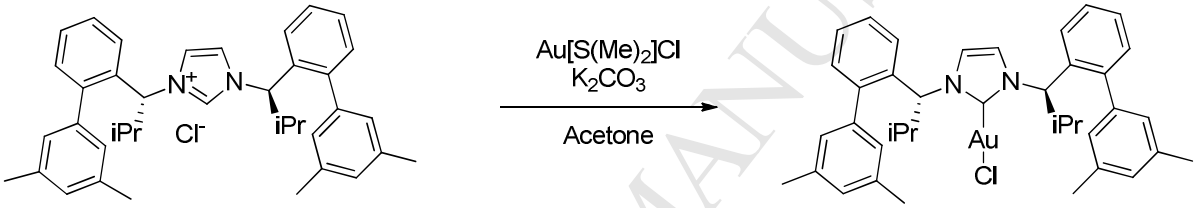
15b (R)-1-(3',5'-dimethyl-[1,1'-biphenyl]-2-yl)-2-methylpropan-1-amine:

Following the general procedure for **15a, 15b** was obtained as a yellow oil (78%). [α] = -15.7 (0.02, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): 7.54 (d, 1H), 7.34 (t, 1H), 7.23 (t, 1H), 7.20 (d, 1H), 7.03 (s, 1H), 6.94 (s, 2H), 3.73 (d, 1H), 2.39 (s, 6H), 1.89 (m, 1H), 0.98 (d, 3H), 0.65 (d, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): 18.6, 18.7, 21.4, 36.7, 64.5, 124.8, 125.5, 126.0, 126.7, 129.0, 129.9, 133.1, 136.0, 138.8, 141.1. LCMS m/z calcd for $C_{18}H_{23}N$ 253.2 found 251.4 (M^+-$2H^+$).



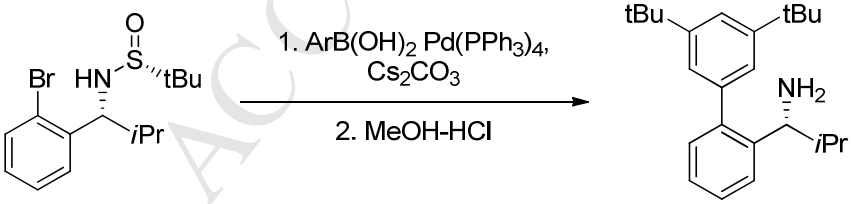
18b 1,3-bis((R)-1-(3',5'-dimethyl-[1,1'-biphenyl]-2-yl)-2-methylpropyl)-1H-imidazol-3-ium chloride:

Following the general procedure for **16a, 18b** was obtained as a brown foam (49%). [α] = -43.2 (0.02, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): 10.62 (s, 1H), 8.32 (d, 2H), 7.55 (t, 2H), 7.34 (t, 2H), 7.27 (s, 1H)7.02 (s, 2H), 6.81 (bs, 3H), 5.30 (s, 4H), 4.88 (d, 2H), 3.47 (m, 3H), 2.32 (bs, 12H), 0.91 (d, 6H), 0.74 (d, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): 142.5, 140.0, 138.2, 135.6, 134.4, 130.1, 129.5, 128.5, 127.4, 127.0, 121.1, 68.8, 31.7, 21.4, 20.2, 20.0. . LCMS m/z calcd for $C_{39}H_{45}N_2Cl$ 576.3 found 541.2 (M^+-Cl^-).



21b (1,3-bis((R)-1-(3',5'-dimethyl-[1,1'-biphenyl]-2-yl)-2-methylpropyl)-2,3-dihydro-1H-imidazol-2-yl)gold(I) chloride:

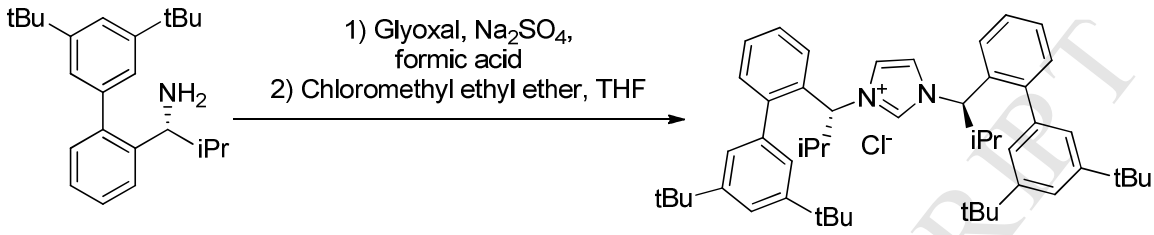
Following the general procedure for **19a, 21b** was isolated as a light yellow solid. (34%). [α] = + 113.6 (0.02, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): 7.72 (d, 2H), 7.42 (t, 2H), 7.33 (t, 2H), 7.26 (s, 2H)7.18 (t, 2H) 7.01 (s, 2H), 6.75 (bs, 2H), 6.71 (s, 2H), 6.44 (bs, 2H), 5.53 (d, 2H), 2.65 (m, 2H), 2.34 (bs, 6H), 2.26 (bs, 6H), 0.93 (d, 6H), 0.77 (d, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): 170.7, 144.8, 139.5, 138.3, 134.8, 131.2, 130.0, 128.1, 127.5, 126.9, 126.7, 118.4, 67.1, 32.3, 21.6, 20.8, 20.4.



15c (R)-1-(3',5'-di-tert-butyl-[1,1'-biphenyl]-2-yl)-2-methylpropan-1-amine:

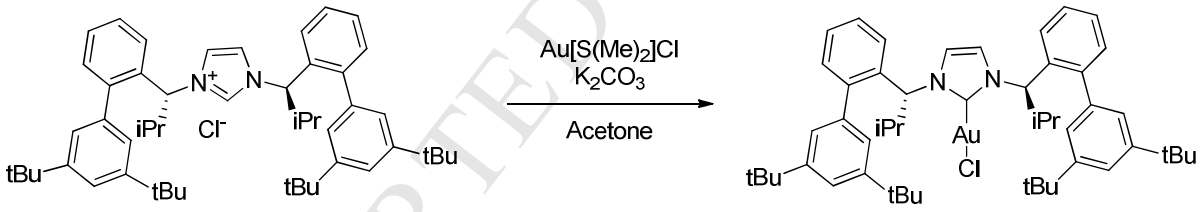
Following the general procedure for **15a, 15c** was obtained as a light orange oil (95%). [α] = -6.7 (0.3, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): 0.64-0.66 (d, 3H), 0.94-0.95 (d, 3H), 1.35 (s, 18H), 1.85-1.89 (m,

1H), 3.64-3.66 (d, 1H), 7.11 (s, 2H), 7.23-7.28 (m, 2H), 7.35-7.39 (m, 2H), 7.50-7.51 (d, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): 19.2, 20.5, 31.5, 31.6, 34.9, 35.11, 57.5, 120.4, 123.9, 126.0, 126.1, 127.6, 129.9, 140.7, 142.8, 143.7, 150.2. . LCMS m/z calcd for $C_{24}H_{35}N$ 337.3 found 360.4 (M^++Na^+).



18c 1,3-bis((R)-1-(3',5'-di-tert-butyl-[1,1'-biphenyl]-2-yl)-2-methylpropyl)-1H-imidazol-3-ium chloride:

Following the general procedure for **16a 18c** was obtained as an orange foam (78%). [α] = -67.1 (0.1, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): 0.67-0.69 (d, 6H), 0.98-0.99 (d, 6H), 1.35 (s, 36H), 6.78-3.80 (m, 2H), 4.70-4.73 (d, 2H), 6.32 (s, 2H), 6.94 (s, 2H), 7.03 (s, 2H), 7.13-7.41 (m, 4H), 7.48 (s, 2H), 7.55-7.56 (t, 2H), 8.38-8.39 (d, 2H), 11.39 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): 20.3, 20.5, 30.7, 31.5, 31.6, 34.9, 35.0, 69.3, 120.5, 120.8, 121.2, 123.9, 127.1, 128.45, 129.6 ,129.8, 130.1, 135.6, 139.6, 142.6. . LCMS m/z calcd for $C_{51}H_{69}N_2Cl$ 745.5 found 710.1 (M^+-Cl^-+H^+).



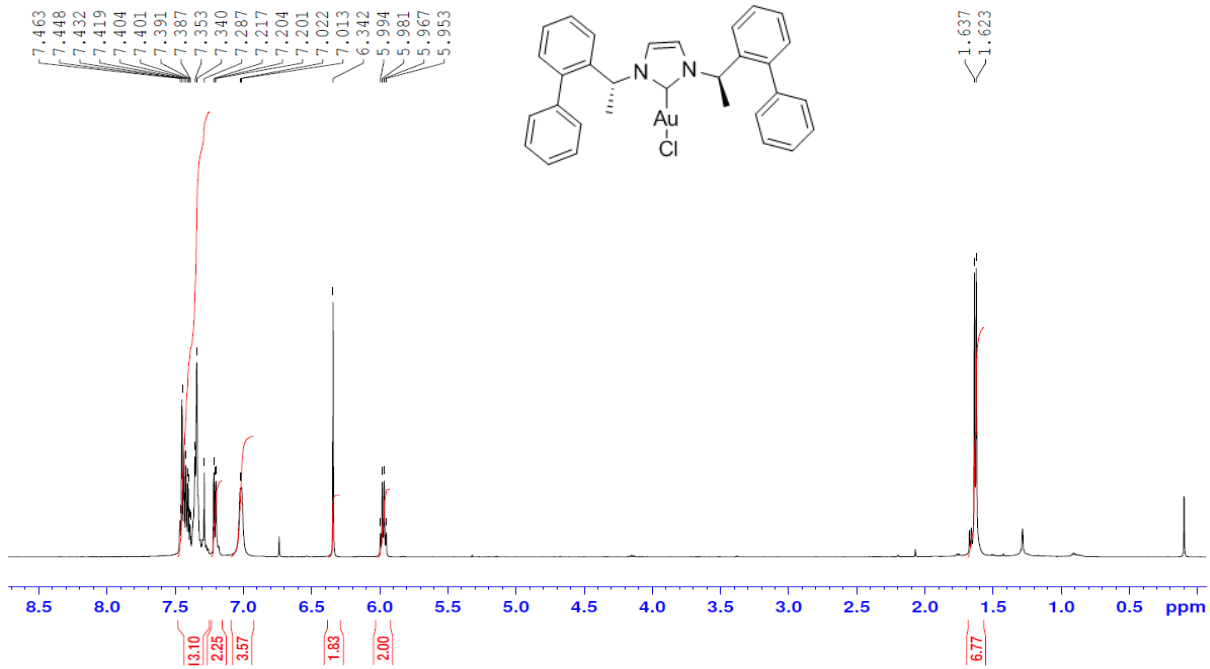
21c (1,3-bis((R)-1-(3',5'-di-tert-butyl-[1,1'-biphenyl]-2-yl)-2-methylpropyl)-2,3-dihydro-1H-imidazol-2-yl)gold(I) chloride:

Following the general procedure for **19a**, **21c** was isolated as a light orange foam (70%). [α] = +97.8 (0.3, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): 0.63-0.65 (d, 6H), 0.98-1.00 (d, 6H), 3.07-3.16 (m, 2H), 5.15-5.193 (d, 2H), 5.98 (s, 2H), 6.7 (bs, 2H), 6.99 (bs, 2H), 7.18-7.43 (m, 6 H), 7.91-7.93 (d, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): 20.3, 20.9, 26.9, 31.5, 68.3, 119.45, 121.7, 123.4, 123.8, 127.6, 127.8, 128.0, 130.5, 134.9, 139.3, 144.6, 168.3.

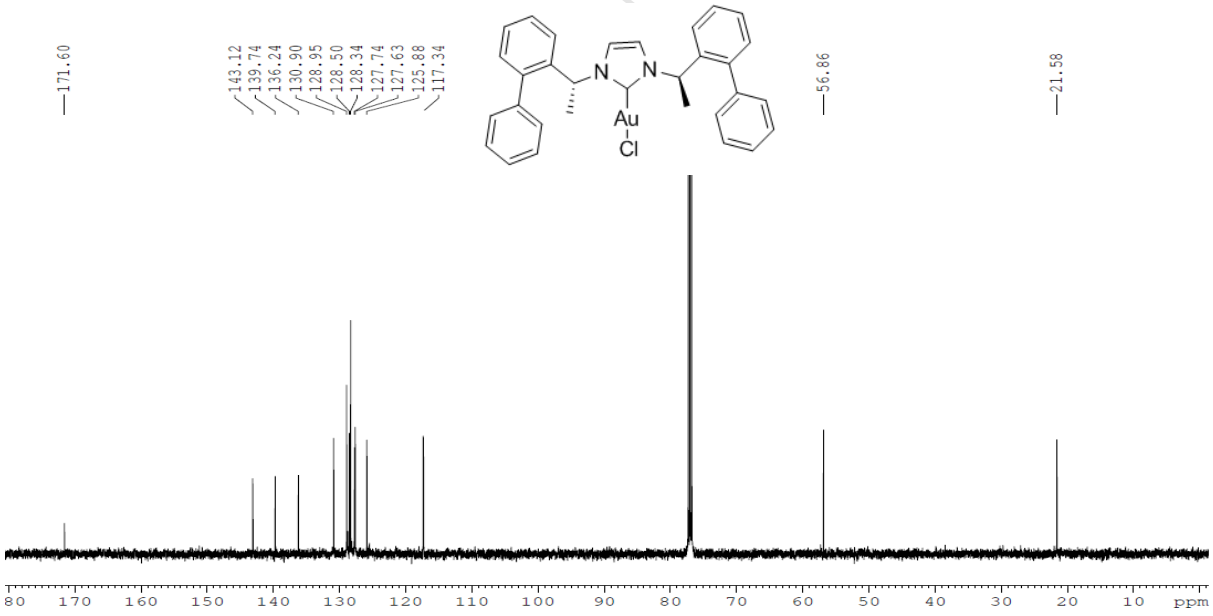
Variable Temperature NMR Experimental Procedure

The ^{1}H NMR spectra were recorded on a 300 MHz instrument with a variable temperature probe. A 0.03 M solution of the sample in deuterated chloroform was placed in a high quality NMR tube. All samples were degassed using a needle to bubble nitrogen through the sample for ~1 minute. The NMR tube was then capped with a cap and sealed with parafilm. The sample tube was placed into the NMR probe and the airline to the probe was replaced with liquid nitrogen transfer line. The desired temperature was set on the variable temperature unit and the sample was allowed to equilibrate for 10 ~ 15 minutes at each set temperature. Then the ^{1}H NMR spectrum at each temperature was recorded.

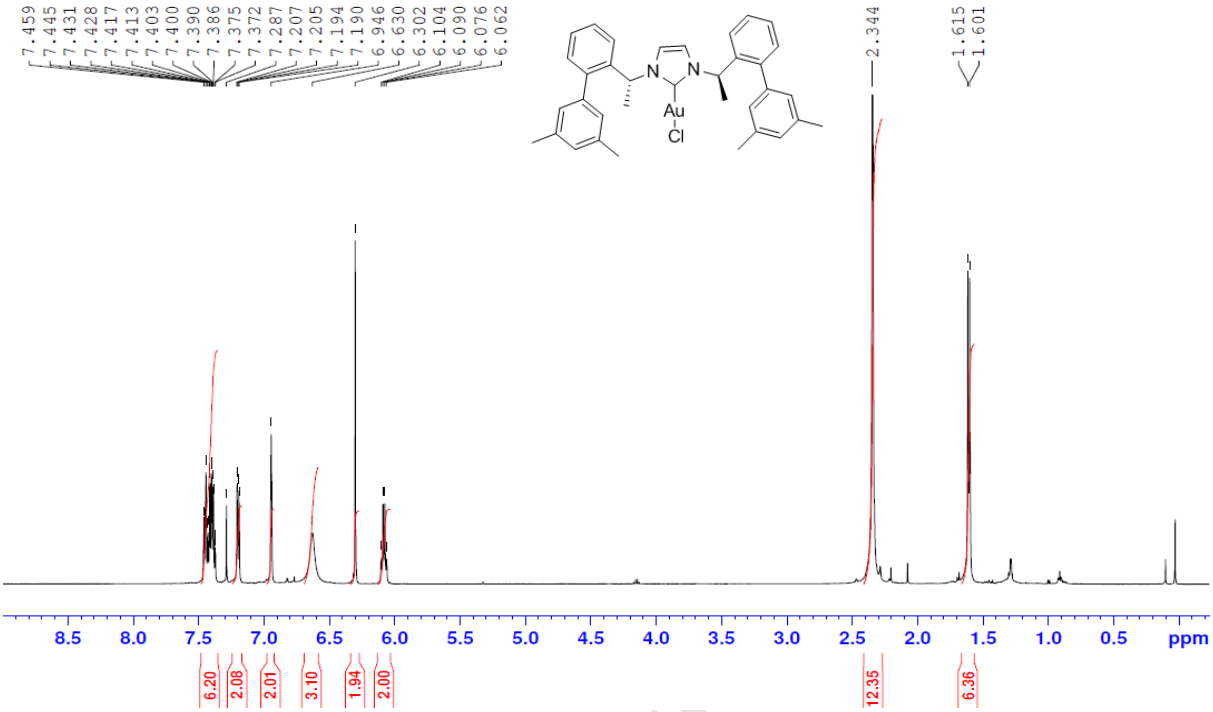
^{1}H NMR 19a



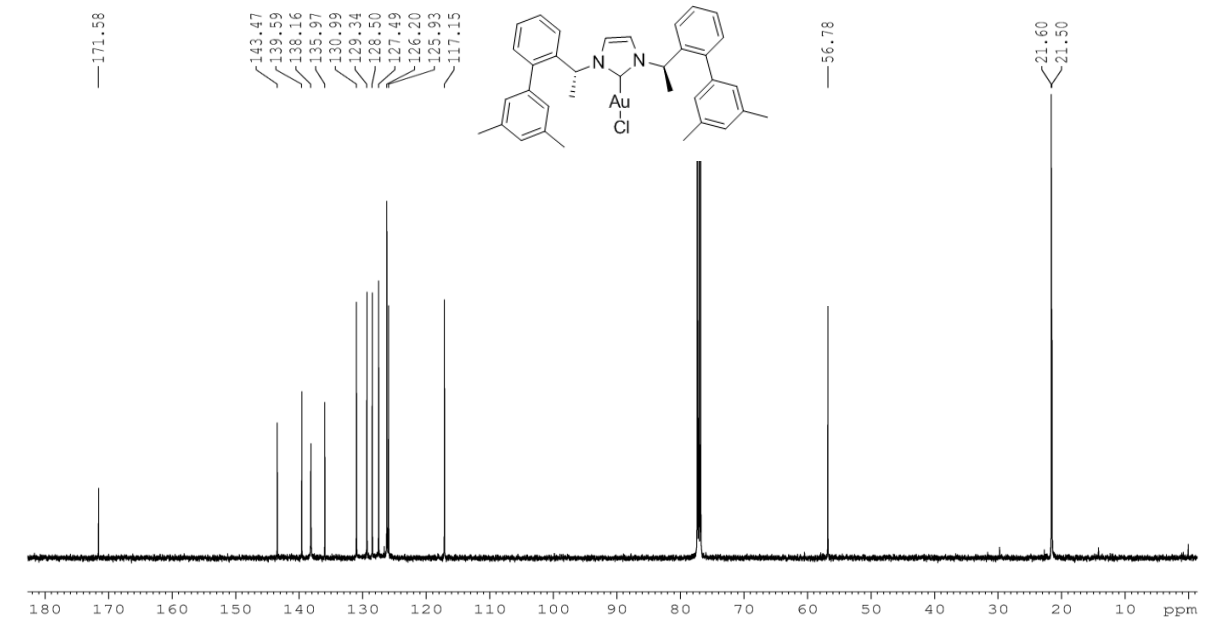
^{13}C NMR 19a



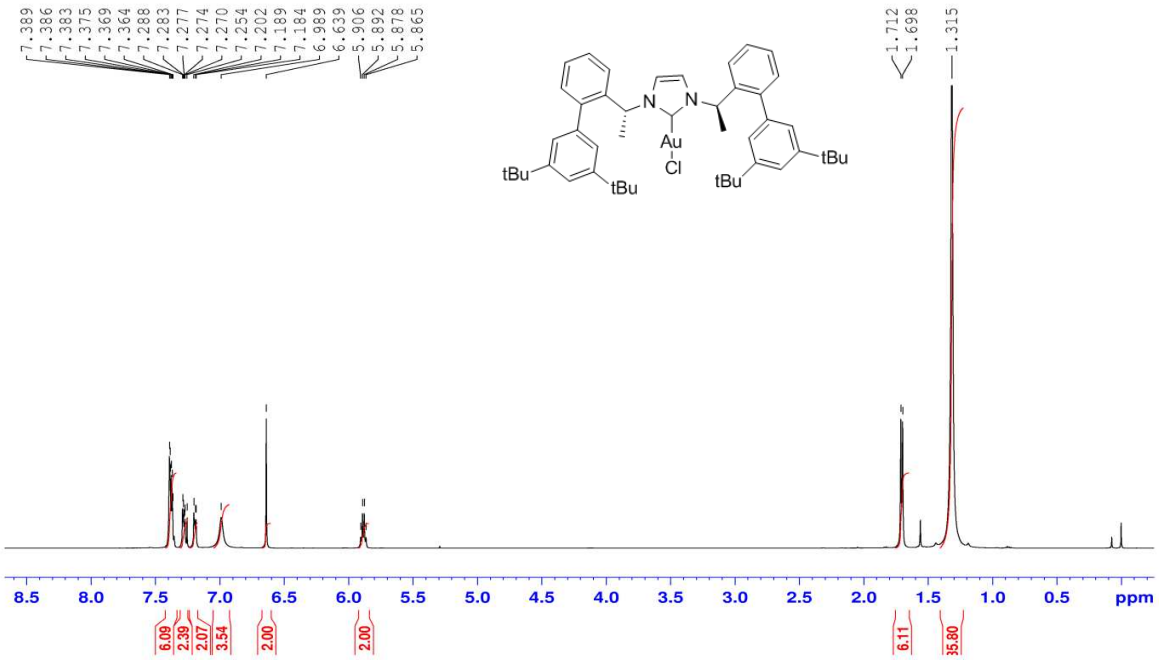
1H NMR 19b



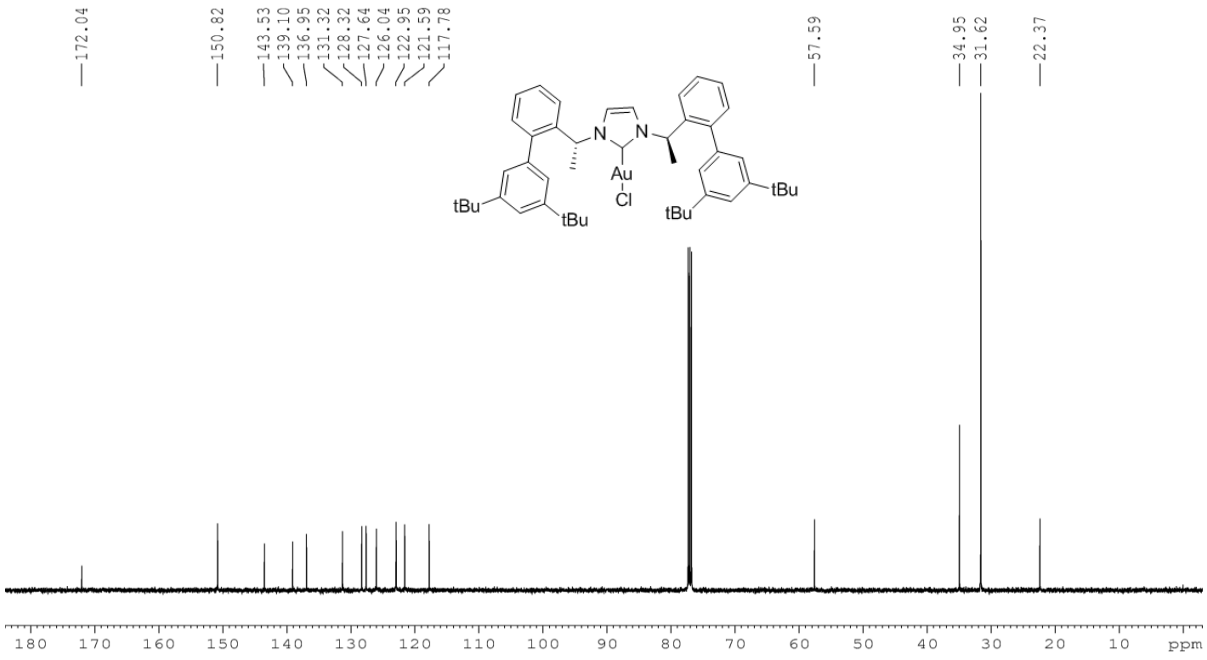
^{13}CNMR 19b



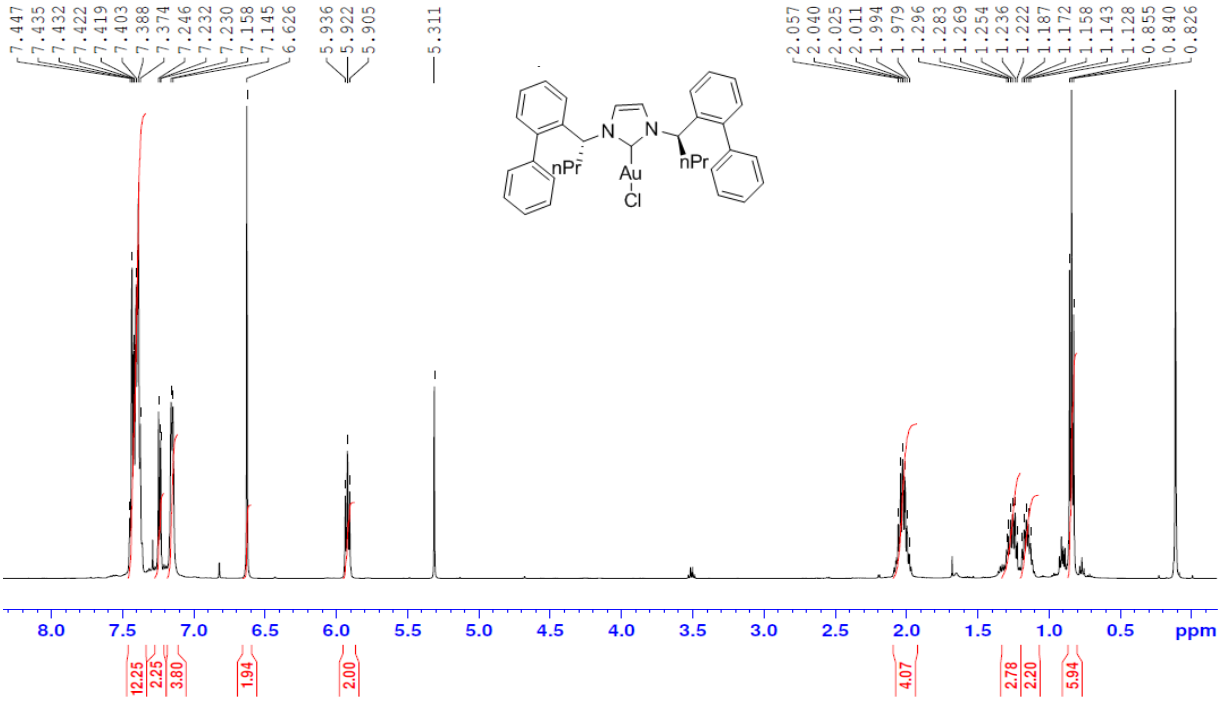
[1]HNMR 19c



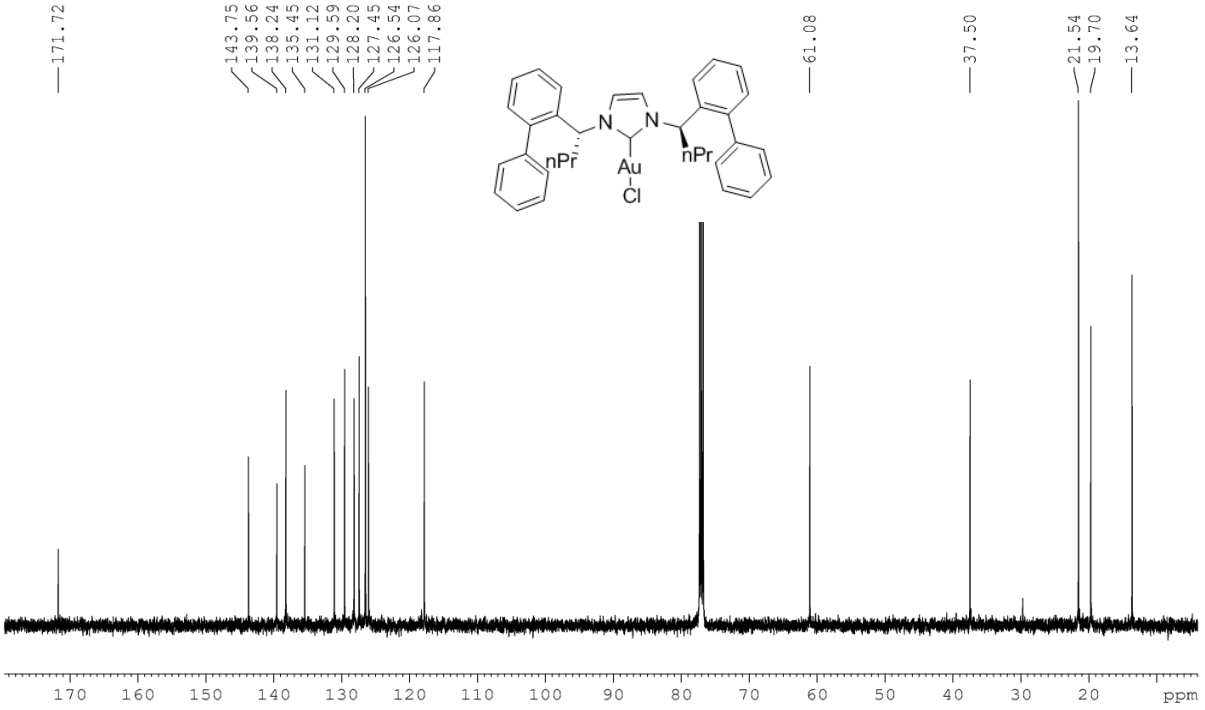
[13]C NMR 19c



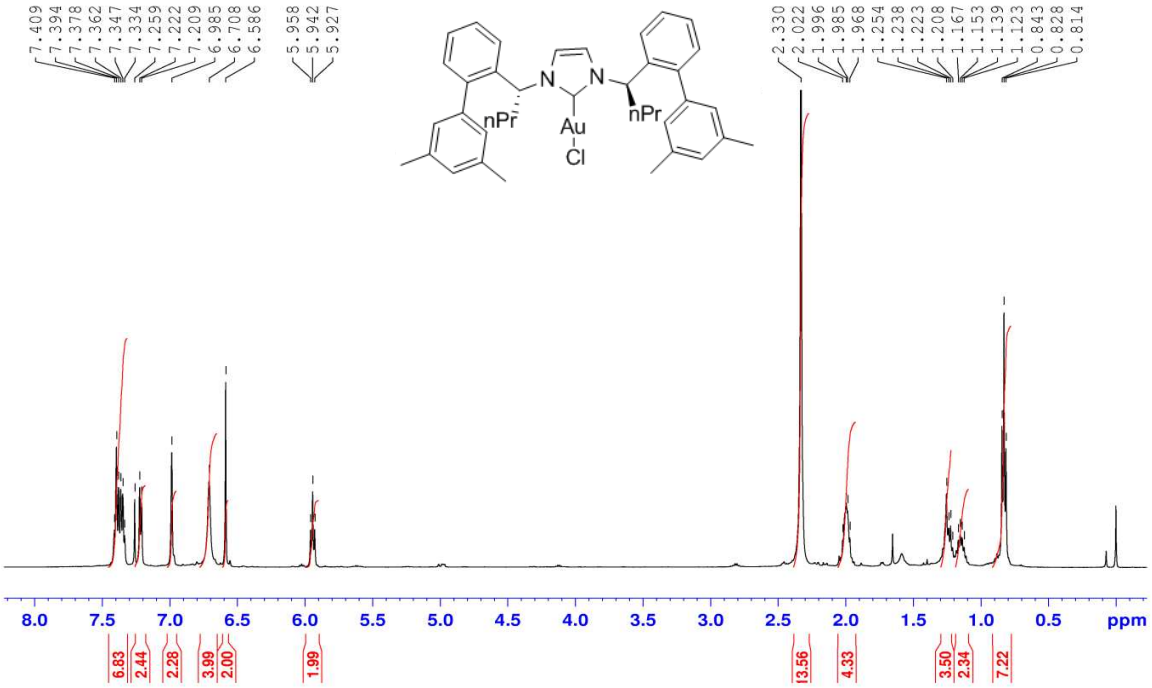
^{1}H NMR 20a



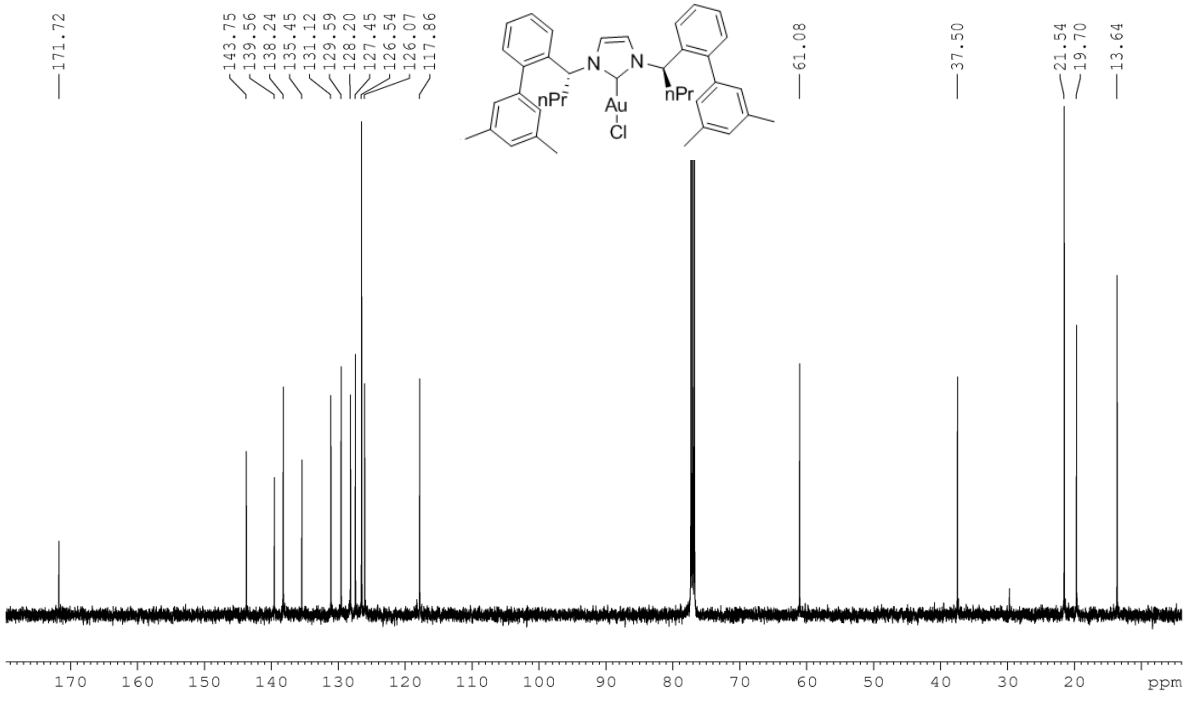
^{13}C NMR 20a



^{1}H NMR 20b



^{13}C NMR 20b



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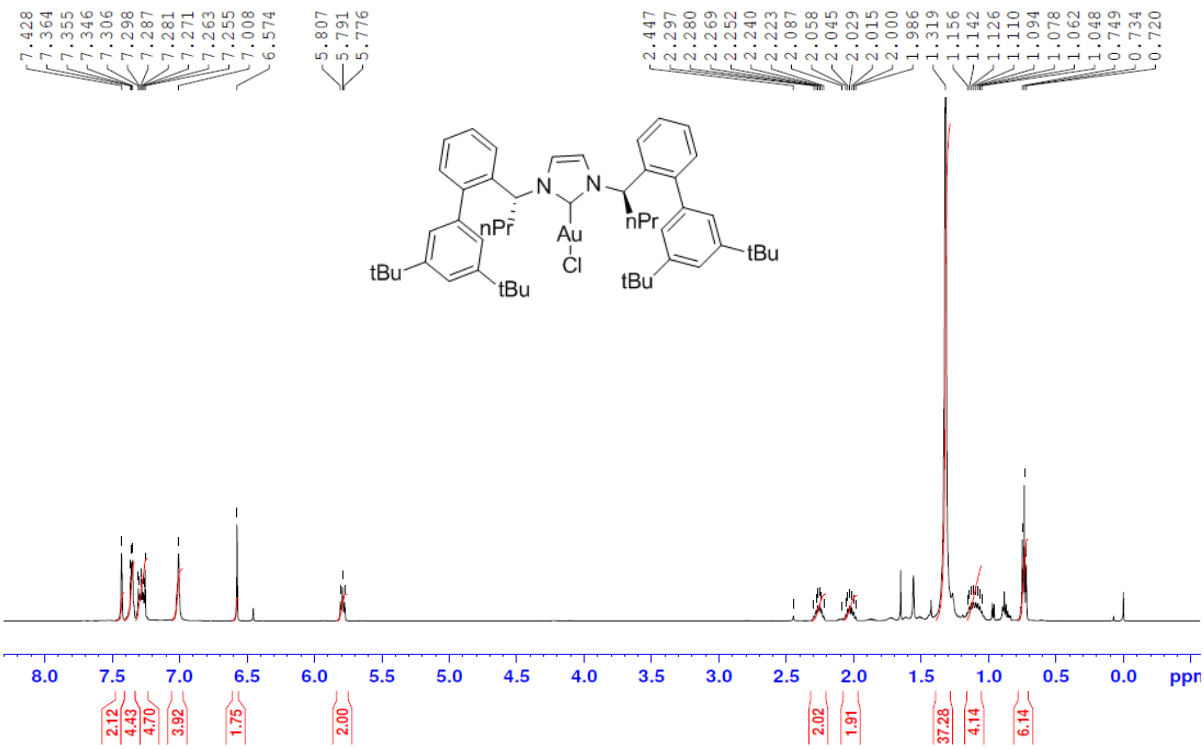
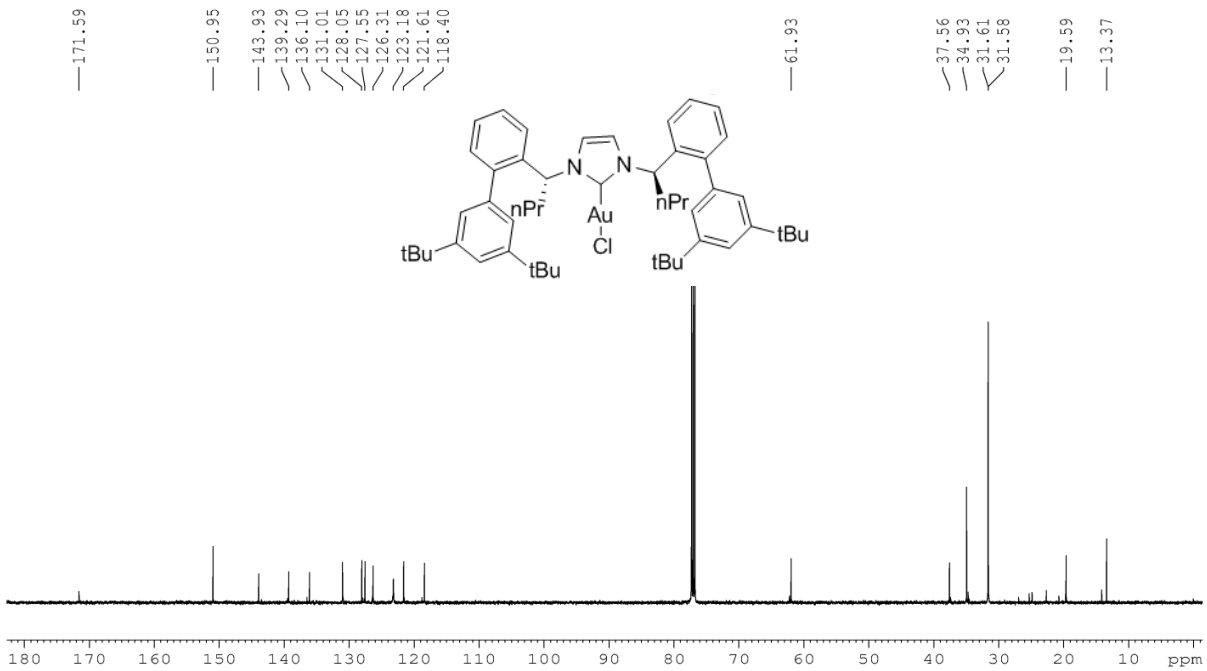
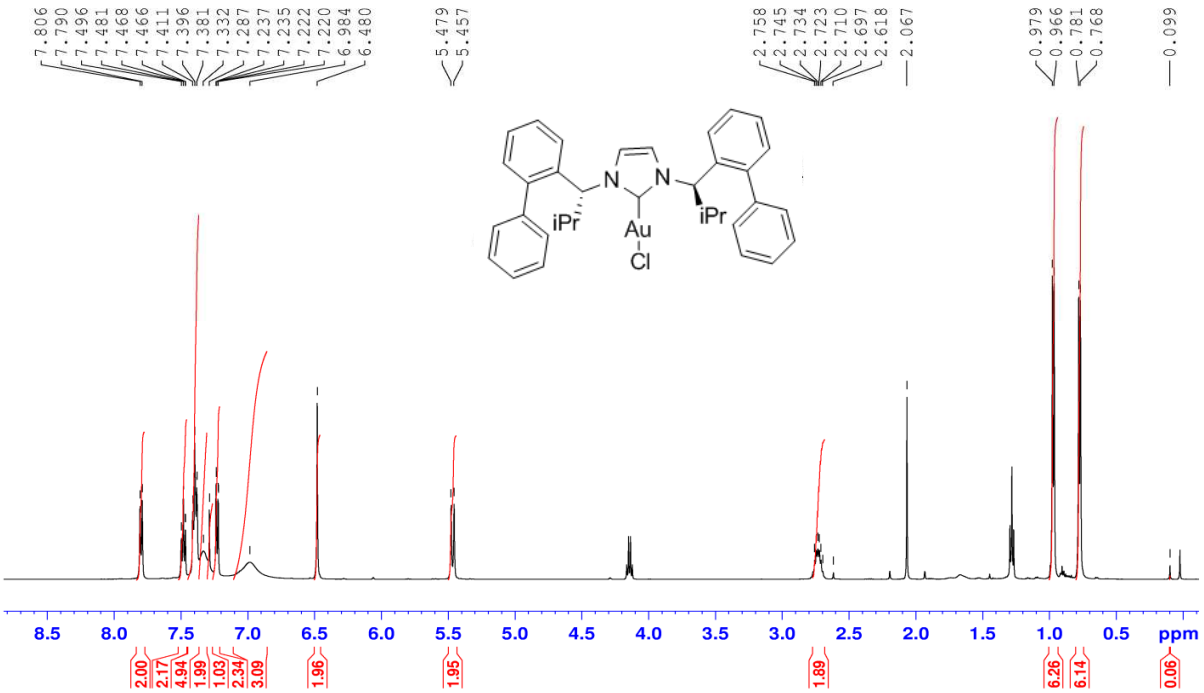


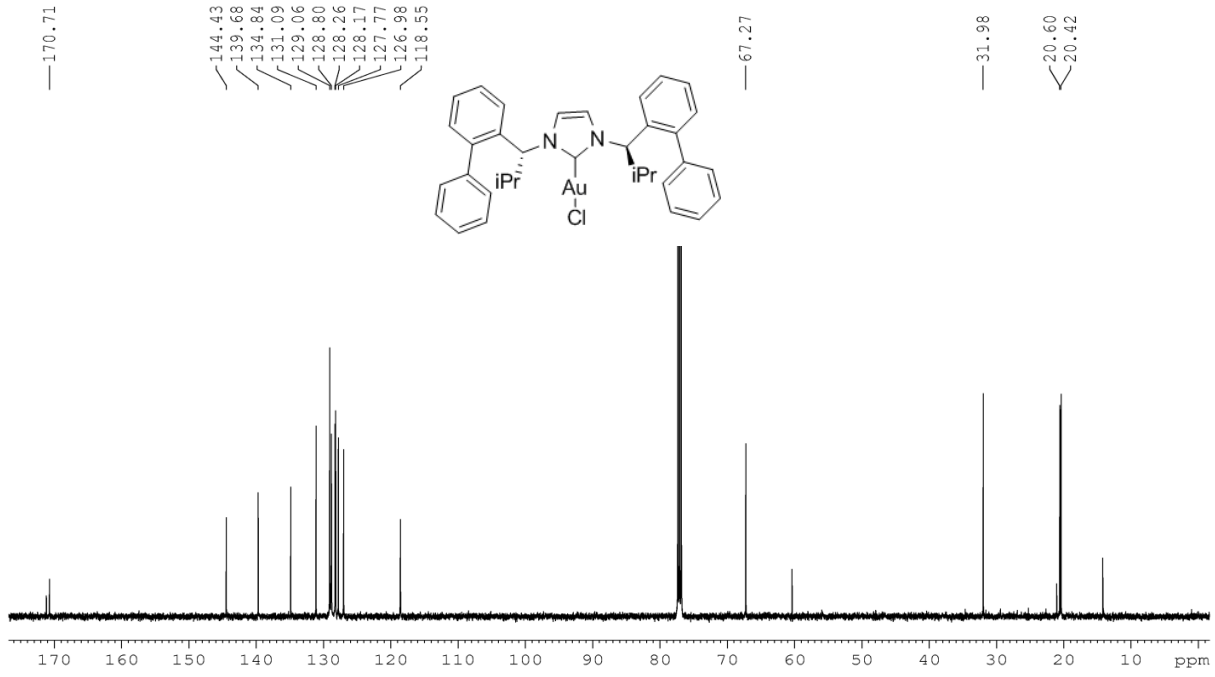
^{13}C NMR 20c



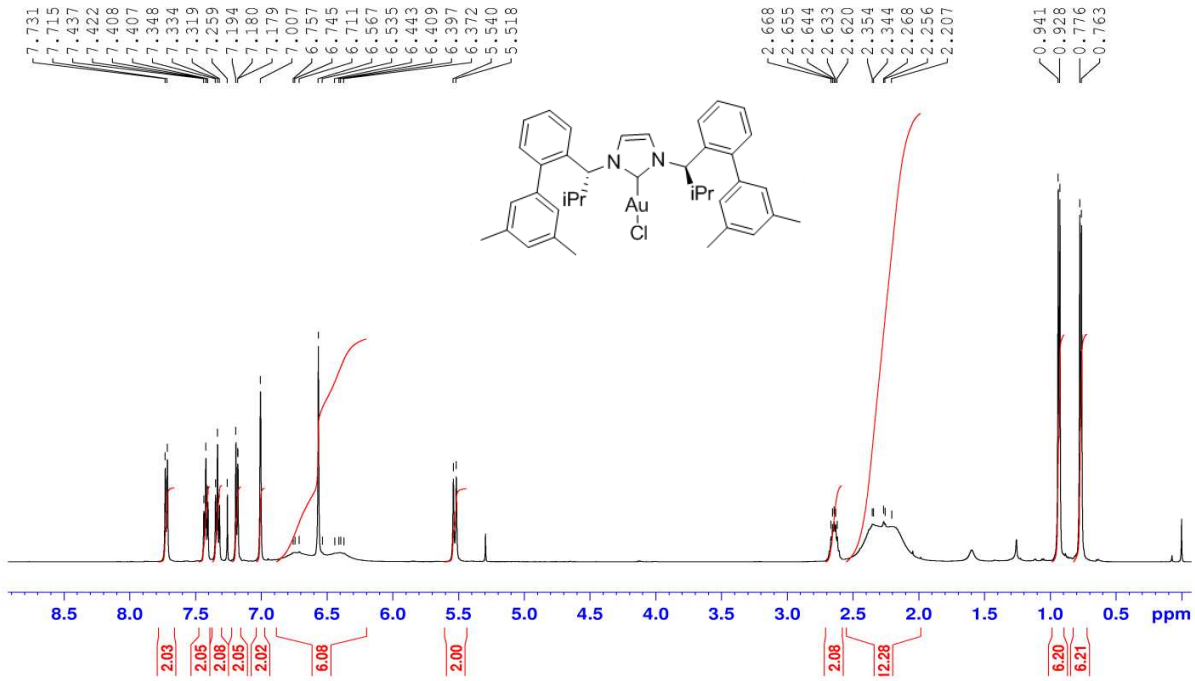
^{1}H NMR 21a



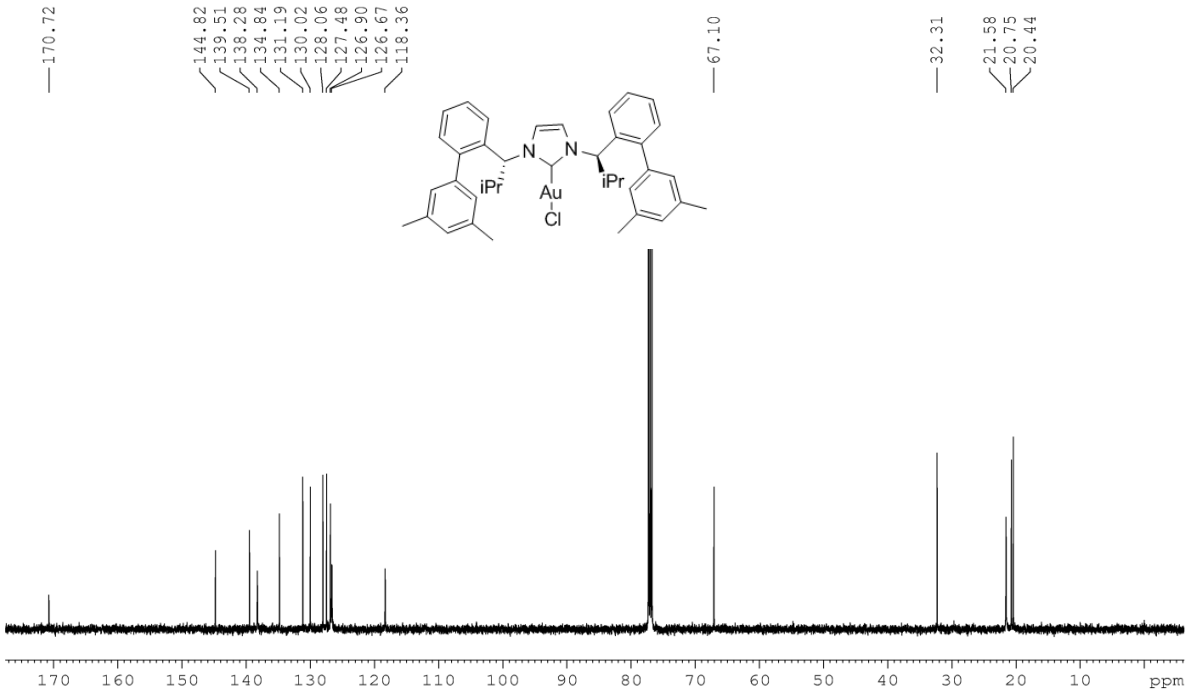
^{13}C NMR 21a



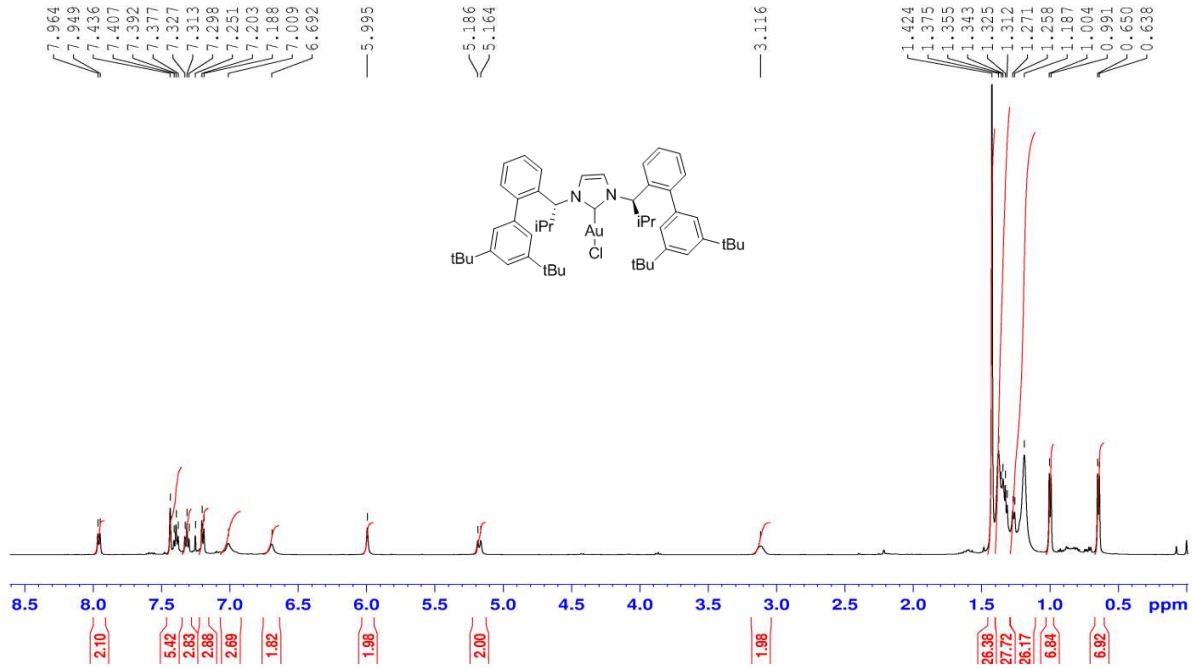
^{1}H NMR 21b



^{13}C NMR 21b



^{1}H NMR 21c



^{13}C NMR 21c

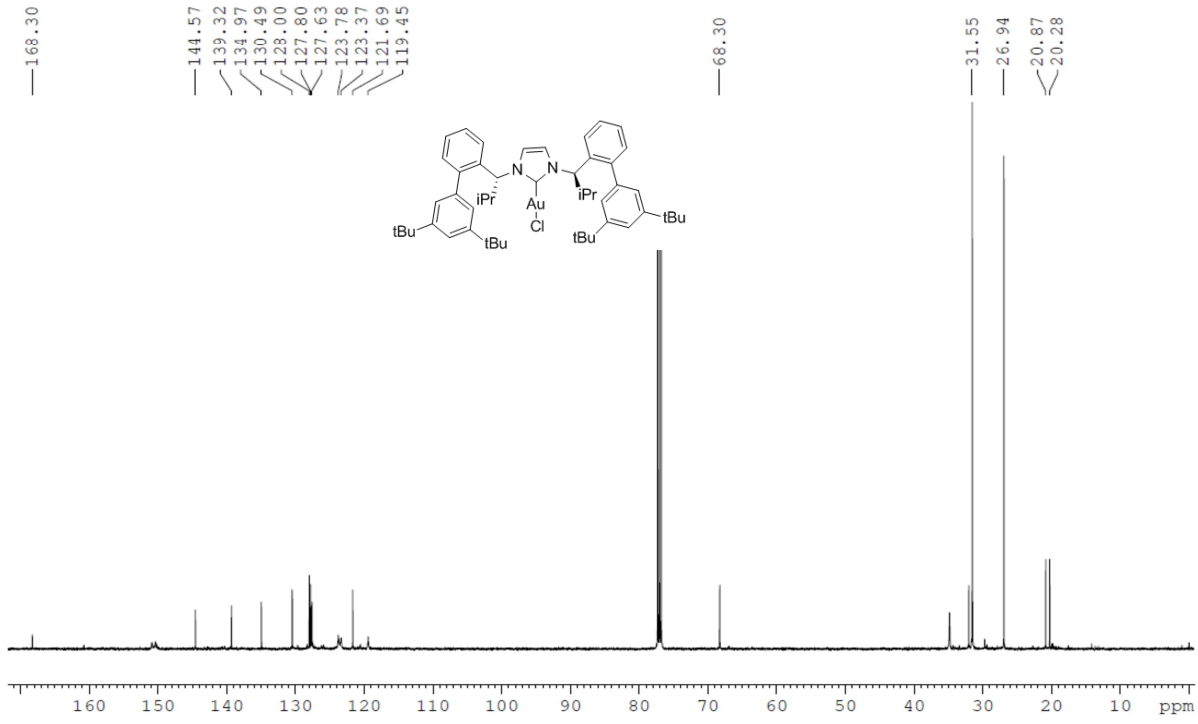


Table 1. Crystal data and structure refinement for 19a.

Identification code	GungAux
Empirical formula	C31 H28 Au Cl N2
Formula weight	660.97
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Tetragonal
Space group	P 41 21 2
Unit cell dimensions	a = 10.4968(18) Å □= 90°.
	b = 10.4968(18) Å □= 90°.
	c = 23.290(4) Å □ = 90°.
Volume	2566.1(10) $Å^3$
Z	4
Density (calculated)	1.711 Mg/m^3
Absorption coefficient	5.860 mm^{-1}
F(000)	1296
Crystal size	0.550 x 0.400 x 0.250 mm^3
Theta range for data collection	2.128 to 27.504°.
Index ranges	-13<=h<=13, -13<=k<=13, -30<=l<=29
Reflections collected	30025
Independent reflections	2954 [R(int) = 0.0278]
Completeness to theta = 25.242°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.32 and 0.20
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2954 / 0 / 161
Goodness-of-fit on F^2	1.097
Final R indices [I>2sigma(I)]	R1 = 0.0113, wR2 = 0.0267
R indices (all data)	R1 = 0.0120, wR2 = 0.0269
Absolute structure parameter	-0.001(3)
Extinction coefficient	n/a
Largest diff. peak and hole	0.299 and -0.591 $e.Å^{-3}$

Table 2. Crystal data and structure refinement for 21b.

Identification code	Gung1214	
Empirical formula	C39 H42 Au Cl N2	
Formula weight	771.16	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 10.3628(14) Å	α= 90°.
	b = 15.568(2) Å	β= 90°.
	c = 20.500(3) Å	γ = 90°.
Volume	3307.1(8) $Å^3$	
Z	4	
Density (calculated)	1.549 Mg/m^3	
Absorption coefficient	4.559 mm^{-1}	
F(000)	1544	
Crystal size	0.550 x 0.450 x 0.350 mm^3	
Theta range for data collection	1.643 to 27.446°.	
Index ranges	-13<=h<=13, -20<=k<=19, -26<=l<=26	
Reflections collected	38394	
Independent reflections	7534 [R(int) = 0.0276]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.30 and 0.24	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7534 / 0 / 396	
Goodness-of-fit on F^2	1.041	
Final R indices [I>2sigma(I)]	R1 = 0.0148, wR2 = 0.0343	
R indices (all data)	R1 = 0.0155, wR2 = 0.0344	
Absolute structure parameter	-0.001(2)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.546 and -0.529 $e.Å^{-3}$	

Table 3. Crystal data and structure refinement for ADC-AuCl 23

Identification code	BGAuCl
Empirical formula	C25 H28 Au Cl N2
Formula weight	588.91
Temperature	173(2) K
Wavelength	0.71073 A
Crystal system, space group	Orthorhombic, P 21 21 21
Unit cell dimensions	a = 9.430(2) A alpha = 90 deg.
	b = 14.582(3) A beta = 90 deg.
	c = 16.947(4) A gamma = 90 deg.
Volume	2330.5(9) A^3
Z, Calculated density	4, 1.678 Mg/m^3
Absorption coefficient	6.440 mm^-1
F(000)	1152
Crystal size	0.50 x 0.25 x 0.15 mm
Theta range for data collection	1.84 to 27.48 deg.
Limiting indices	-12<=h<=12, -18<=k<=18, -21<=l<=21

Reflections collected / unique	27013 / 5287 [R(int) = 0.0307]
Completeness to theta = 27.48	99.3 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.45 and 0.23
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5287 / 0 / 266
Goodness-of-fit on F^2	1.028
Final R indices [I>2sigma(I)]	R1 = 0.0153, wR2 = 0.0336
R indices (all data)	R1 = 0.0164, wR2 = 0.0338
Absolute structure parameter	-0.005(5)
Largest diff. peak and hole	0.472 and -0.558 e.A^-3

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