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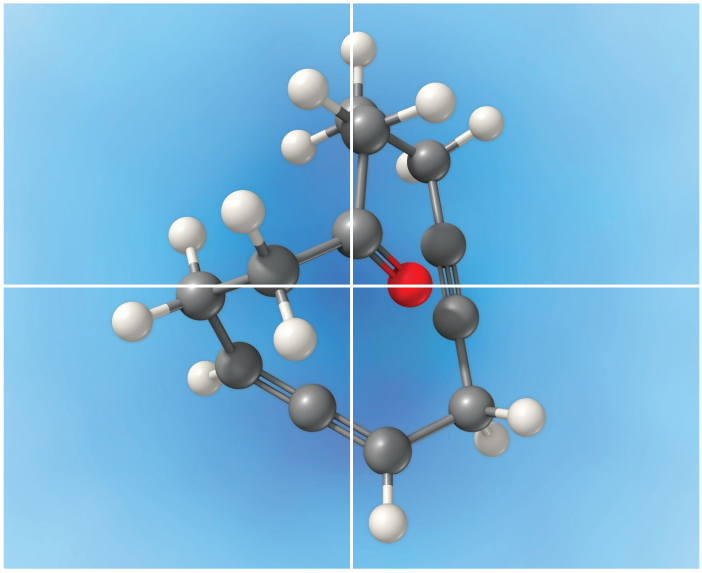

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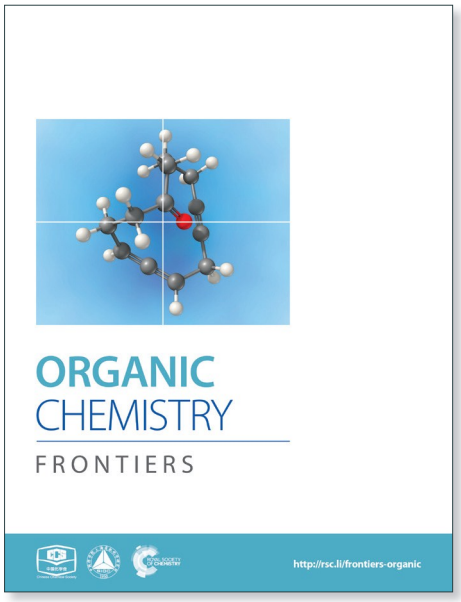

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Cite this: DOI: 10.1039/c0xx00000x

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ARTICLE TYPE

Selectfluor promoted NHC-Oxazoline gold(I) complexes catalyzed cycloaddition/oxidation reaction of enynones with alkenes

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

The *ortho*- and *meta*-substituted NHC-oxazoline ligands based on phenyl scaffold have been synthesized in a six-step pathway, and their coordination with Au(Me_2S)Cl gave the corresponding NHC-gold(I) complexes in good yields. Resulting from restricted rotation between the phenyl ring and the benzimidazole ring, the *ortho*-substituted NHC-oxazoline gold(I) complexes exhibited as a pair of diastereomers, and their structures have been further confirmed by X-ray diffraction analysis. Moreover, combination of these gold(I) complexes with Selectfluor in situ was used to catalyze the reaction of enynone with alkenes using air as oxidant to give naphthalene derivatives in moderate to excellent yields. Some of controlled experiments were carried out to reveal the active species as chelated NHC-oxazoline gold(I) species and the role of Selecfluor played in this reaction.

Introduction

The first decade of the century has witnessed the exploration of homogeneous gold chemistry.[1] Owing to the character as soft carbophilic Lewis acid towards C-C multiple bonds, these homogeneous gold complexes have been successfully applied as pivotal catalysts for enyne cyclization reactions. Among the various factors of gold-catalyzed reactions, the ligands play a decisive role on the catalytic activities. The *N*-heterocyclic carbene (NHC) ligands have been widely applied as a sort of metal ligands, which could connect to various main and transition metals.[2] The NHC-gold complexes have showed dramatically different catalytic activities and selectivities compared to other normally used phosphine ligands[3] due to that the NHC ligands exhibited stronger σ-donor but weaker π-acceptor abilities.[4] Thus, developing highly efficient NHC-gold catalysts is an urgent and significant work.

In the past few years, numerous of NHC-gold(I) complexes have been synthesized and successfully applied in metal-catalyzed homogeneous reactions, even for some challenging reactions in which other catalysts exhibited bad catalytic activities.[5] In comparison, the synthesis and application of NHC-gold(III) complexes received less attention despite the Fehlhammer's group firstly reported the synthesis of NHC gold(III) complexes in 1974.[6] Later, the Raubenheimer's group revealed another synthetic method of NHC-gold(III) complexes by oxidative addition of halogens to the NHC-gold(I) complexes.[7] Several synthesized NHC-gold(III) complexes have been applied in gold-catalyzed reactions. Unfortunately, few of these gold(III) complexes exhibited good catalytic activities.[8] Some typical examples of NHC-gold(I) and NHC-gold(III) complexes were presented in Figure 1.[9]

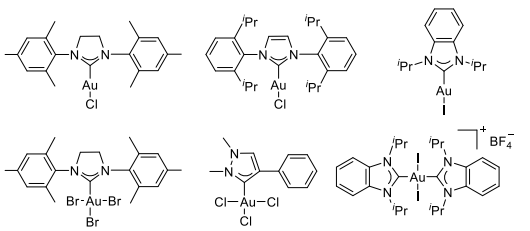

Figure 1. Typical NHC-gold(I) and NHC-gold(III) complexes

In consideration of the linear coordination of gold(I) complexes, the corresponding NHC ligands connected with gold(I) atom were always designed as monodentate ligands. Even for the multiple-coordinated gold(III) atoms, the polydentate NHC ligands ligated gold(III) complexes were also rare on account of the limited synthetic methods. But for some gold-catalyzed reactions, the multiple-ligands coordinated gold complexes exhibited better catalytic activities than traditional monodentate ligands connected gold complexes. Recently, Shi's group has developed a series of 1,2,3-triazole-coordinated phosphine-gold(I) complexes to catalyze challenging chemical transformations, achieving some excellent results.[10] The Hashmi's group disclosed the synthesis of chelated bidentate Pic$AuCl_2$ complexes. This

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† Electronic supplementary information (ESI) available: X-Ray crystallographic data (CIF) for **8a** (CCDC 973292) and **10c** (CCDC 950237) and ^{1}H NMR and ^{13}C NMR spectra of all the complexes. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b000000x/

new gold(III) complex was also used in many homogenous reactions and exhibited outstanding catalytic activities.[11] Inspired by recent developments of multiple-coordinated gold complexes, we were intrigued by the synthesis of polydentate functionalized NHC ligands ligated gold(I) or gold(III) atoms to seek out more active gold catalysts.

Selectfluor has been frequently used to oxidize gold(I) species to the gold(III) species even though the specific oxidation process was still ambiguous.[12] Therefore, we assumed to design a bidentate NHC-oxazoline ligands **A** and make them ligated with gold(I) species. According to the previous literature, these oxazoline substituted NHC-gold(I) complexes **B** should be transformed to chelated NHC-oxazoline gold (III) complexes **C** upon treatment with Selectfluor (Figure 2). In this paper, we would like to report a novel performance of Selectfluor to make the NHC-gold(I) complex **B** being transformed to the ionic chelated NHC-oxazoline gold(I) complex **D**. This in situ generated gold(I) species were used to catalyze the reaction of enynone with alkenes using air as oxidant to give naphthalene derivatives in moderate to excellent yields.

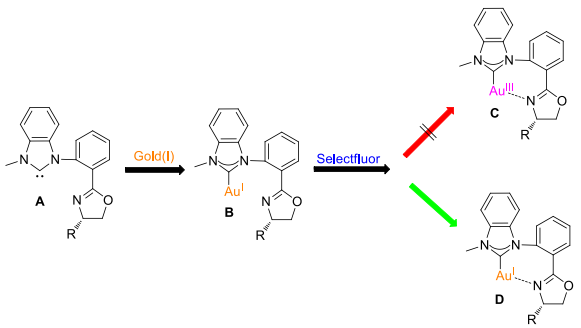
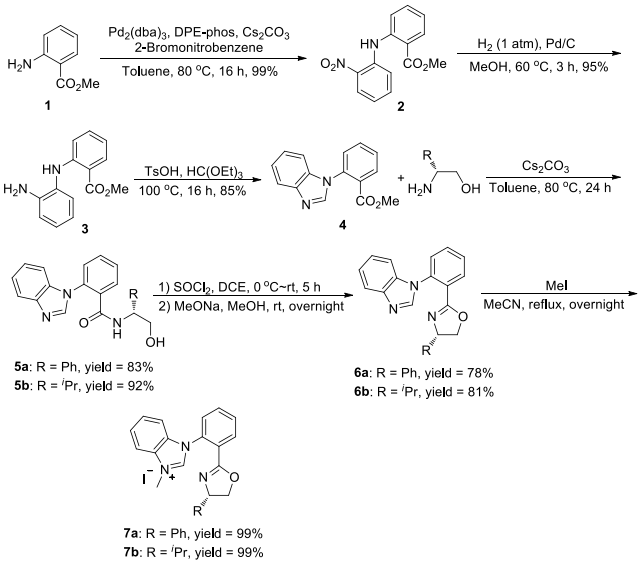


Figure 2. Design of NHC-oxazoline gold species

Results and discussion

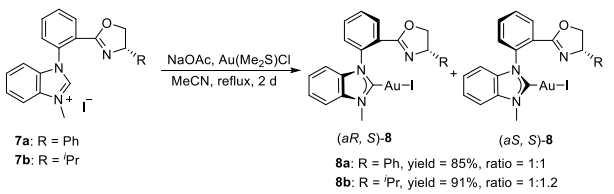
Preparation of *ortho*-substituted NHC-oxazoline gold(I) complexes

The synthesis of *ortho*-substituted benzimidazolium salts based on phenyl ring started from the methyl anthranilate. Namely, compound **1** was used to react with 2-bromonitrobenzene in the presence of DPE-phos-Pd(OAc)$_2$ catalyst and Cs_2CO_3 to give the Buchwald-type coupling product **2** in quantitative yield. Then, treatment of compound **2** with Pd/C under hydrogen atmosphere afforded the corresponding hydrogenation product **3** in 85% yield. The benzimidazole derivative **4** could be obtained by simple cyclization of compound **3** with triethyl orthoformate and a catalytic amount of TsOH at 100 ^{o}C. Consequently, the compound **4** was utilized to react with two different kinds of chiral aminoalcohols promoted by Cs_2CO_3 in toluene to give the corresponding amide derivatives **5** in good yields, which further reacted with thionyl chloride and MeONa in methanol respectively via halogenation/cyclization reaction to give the desired benzimidazole-oxazoline products **6** in good yields. Finally, combination of **6** with methyl iodide in acetonitrile under reflux afforded the carbene precursors **7** with high yields, which could be directly used to next step without any further purification (Scheme 1).



Scheme 1. Synthesis of *ortho*-substituted NHC-oxazoline ligands

With the carbene precursors **7** in hand, we turned our attention to the synthesis of NHC-oxazoline gold(I) complexes. Treatment of benzimidazolium salt **7a** with Au(Me$_2$S)Cl in the presence of NaOAc in acetonitrile under reflux generated the corresponding NHC-gold(I) complex **8a** in high yield (Scheme 2). ^{1}H NMR spectra of complex **8a** revealed two sets of alkyl group signals with equal ratio. Same process was operated with the isopropyl substituted benzimidazolium salt **7b** to afford the corresponding NHC-oxazoline gold(I) complex **8b** in good yield as well. However, the isomeric ratio of complexes (*aS, S*)-**8b** and (*aR, S*)-**8b** was 1.2:1 on the basis of ^{1}H NMR spectroscopic data, presumably due to the steric influence of the oxazoline group.[13]



Scheme 2. Synthesis of *ortho*-substituted NHC-oxazoline gold(I) complexes

The structures of complexes **8** were confirmed by the X-ray diffraction of complex **8a**. The suitable single crystal of complex **8** could be obtained from the mixed solvents of dichloromethane and ethyl ether. Furthermore, the structures of two isomers, (*aS, S*)-**8a** and (*aR, S*)-**8a,** were both confirmed by the X-ray diffraction data in one crystal cell as a pair of diastereoisomer. The ORTEP drawing is shown in Figure 3 and the CIF data are presented in the Supporting Information. According to the X-ray diffraction data, only the benzimidazole carbene rather than the oxazoline group is coordinated with gold atom. When the benzimidazole group was ligated with gold atom, the free rotation of the bond between the phenyl ring and the benzimidazole ring is blocked, causing the appearance of the axial chirality.

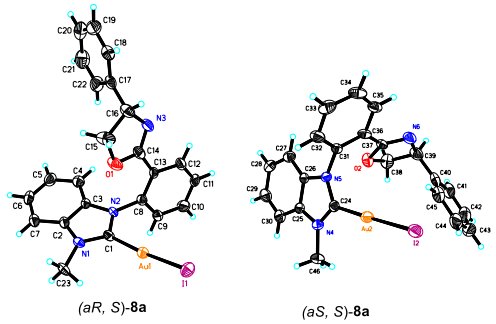
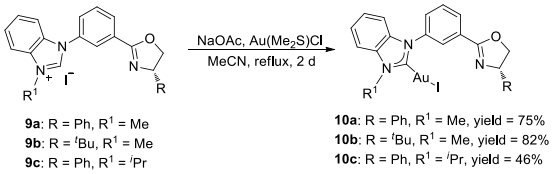


Figure 3. Molecular structure of complexes (*aR*, *S*)-**8a** and (*aS*, *S*)-**8a**. Ellipsoids are shown at 30% probability. Selected bond lengths [Å] and angles [°] of complex (*aR*, *S*)-**8a** and (*aS*, *S*)-**8a**: Au1-C1 2.000(7), Au2-C24 1.999(7), N1-C1 1.321(9), N4-C24 1.328(9), O1-C14 1.336(10), N3-C14 1.247(10), N6-C37 1.282(11), C1-Au1-I1 171.9(2), C24-Au2-I2 178.1(2), C1-N1-C2 111.2(6), N1-C1-N2 107.0(6), C24-N4-C25 111.0(6), N3-C14-O1 117.8(9), N4-C24-N5 106.6(6).

Preparation of *meta*-substituted NHC-oxazoline gold(I) complexes

According to our previous work,[14] the *meta*-substituted benzimidazolium salts **9** could be obtained smoothly. Treatment of these carbene precursors with gold species and base in the same method as that mentioned above afforded the corresponding NHC-oxazoline gold(I) complexes **10** in good yields (Scheme 3). The ^{1}H NMR spectra of complexes **10** showed only one set of alkyl signals, suggesting that the structures of complexes **10** were completely different from those of NHC-gold(I) complexes **8**.



Scheme 3. Synthesis of *meta*-substituted NHC-oxazoline gold(I) complexes

The accurate structures of complexes **10** were also disclosed by the X-ray diffraction of NHC-oxazoline gold(I) complex **10c**. The high quality single crystal for X-ray diffraction was obtained from the mixed solvents of petroleum ether and dichloromethane. The ORTEP drawing is shown in Figure 4 and the CIF data are summarized in the Supporting Information. As for the NHC-oxazoline gold(I) complexes **10c**, the gold atom was only ligated with the NHC ligand, and the oxazoline group did not participate in the ligation process.

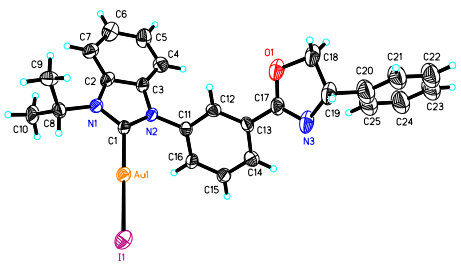
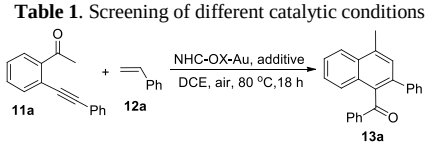


Figure 4. Molecular structure of complex **10c**. Ellipsoids are shown at 30% probability. Selected bond lengths [Å] and angles [°] of complex **10c**: Au1-C1 2.018(8), Au1-I1 2.5459(8), N1-C1 1.343(9), C17-N3 1.28(3), C17-O1 1.35(3), N1-C8 1.483(10), C1-Au1-I1 176.8(2), C1-N1-C2 109.5(6), N2-C1-N1 107.6(7), N2-C1-Au1 125.2(6), N3-C17-O1 114(2).

The Selectfluor promoted NHC-oxazoline gold(I) complexes catalyzed cycloaddition/oxidation reaction

With all these NHC-oxazoline gold(I) complexes in hand, our attention was turned to investigate the catalytic activities of these oxazoline-substituted NHC-gold(I) complexes in the presence of Selectfluor. The gold-catalyzed cycloaddition/oxidation reaction of enynone with alkenes, which was realized as one important kind of methods to synthesize the multiple-substituted naphthalene derivatives, has already been reported widely.[15] Recently, Zhu's group disclosed the in situ generated NHC-gold(III) catalyzed cycloaddition of enynone with two kinds of alkenes to afford the corresponding cyclohexane derivatives in good yields under mild conditions.[16] At the end of this work, they presented the cycloaddition/oxidation reaction under oxygen atmosphere to afford the aromatization product with moderate yield. Therefore, we decided to use our NHC-oxazoline gold(I) complexes to optimize this reaction. Initially, enynone **11a** and styrene **12a** were chosen as substrates for the model reaction. Treatment of these substrates with NHC-oxazoline gold(I) complex **8a** (5 mol%) and Selectfluor (15 mol%) in dichloroethane at 80 °C under air atmosphere (1.0 atm) furnished the corresponding naphthalene derivative **13a** in 92% yield (Table 1, entry 1). The absence of Selectfluor caused that the yield of **13a** in the same reaction significantly decreased (Table 1, entries 2 and 3). The in situ generated NHC-gold(I) species in the presence of $AgSbF_6$ caused the reaction system become complex (Table 1, entry 4). The reaction could not take place only in the presence of Selectfluor (Table 1, entry 5). All the experiments disclosed the indispensability of the NHC-gold(I) complex and the Selectfluor in the reaction. Next, other NHC-oxazoline gold(I) complexes were selected to test their catalytic activities in this reaction, furnishing the naphthalene derivative **13a** in 29-83% yields (Table 1, entries 6-9). The NHC-oxazoline gold(I) complex **8a** functioned better than others which was confirmed as the best catalyst in this reaction.

Table 1. Screening of different catalytic conditions

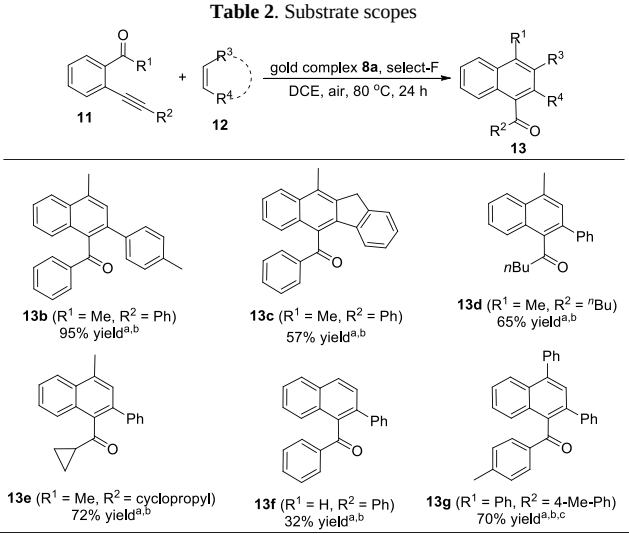


entry[a]	Au-cat	additive	yield (%)[b]
1	**8a**	select-F	92
2	**8a**	-	15
3	**10a**	-	trace
4	**8a**/$AgSbF_6$ (5 mol%)	-	complex
5	-	select-F	no reaction
6	**8b**	select-F	83
7	**10a**	select-F	63
8	**10b**	select-F	29
9	**10c**	select-F	77

a) Substrate **11a** (0.1 mmol) and **12a** (0.5 mmol) were stirred in DCE (2 mL) at 80 °C for 18 h using 5 mol% gold catalyst and 15 mol% Selectfluor as the catalytic system under air atmosphere; b) Isolated yield.

With the optimized reaction conditions in hand, the substrate scope was then examined. Some typical substrates have been chosen to apply in this catalytic process and the results are shown in Table 2. Firstly, various styrene derivatives could successfully react with enynone **11a** to give the desired products in moderate to excellent yields. This reaction was slightly sensitive to the steric hindrance of alkene. For example, the indene participated reaction could only furnish the fused-ring product **13c** in 57% yield. Next several enynone derivatives were chosen to test this catalytic system. The terminal groups of alkyne moiety were changed to *n*-butyl and cyclopropyl groups, which also smoothly furnished the corresponding products **13d** and **13e** in good yields. Finally, the substituted groups of carbonyl moiety were examined. The highly active enynal derivative **11f** could be used to react with styrene, affording the corresponding product **13f** in 32% yield. The reactivity of more sterically hindered phenyl-substituted enynone **11g** was poor, and its reaction should be carried out under oxygen (1.0 atm) atmosphere for 72 h in 1,2-dichloroethane to give the desired polycyclic aromatic product **13g** in 70% yield.

Table 2. Substrate scopes



a) Substrates **11** (0.1 mmol) and **12** (0.5 mmol) were stirred in DCE (2 mL) at 80 °C for 24 h using 5 mol% gold catalyst and 15 mol% oxidant as the catalytic system under air atmosphere;
b) Isolated yield;
c) This reaction was performed under oxygen atmosphere (1.0 atm) for 72 h.

Next, we turned our attention to reveal the accurate structure of NHC-oxazoline gold species. Unfortunately, the NHC-oxazoline gold complex **14** could not be purified by column chromatography or upon recrystallization because they are quite labile and unstable. Firstly, the ^{19}F NMR spectrum of the active gold species showed the existence of BF_4^- anion which indicated the active species probably was an ionic complex (see Supporting Information). Next, we started to investigate the coordination state of the oxazoline group through its ^1H NMR spectrum because the chemical shift of **Ha** and **Ha'** atom ligated with chiral carbon in oxazoline moved to the low field when the oxazoline group connected with metal atom.[17] After combination of complex **8a** with 2.0 equivalent of Selectfluor in $CDCl_3$, the mixture was stirred at room temperature for 5 min and then its ^1H NMR spectrum was directly measured. The typical double signal sets of complex **8a** vanished since in the alkyl area, only one group of alkyl signals could be identified. Besides, the chemical shift of **Ha''** atom ligated with chiral carbon atom in oxazoline moiety moved from the 5.1 ppm to the 5.9 ppm (Figure 5) which strongly supported the generation of chelated structure. As for *meta*-substituted NHC-gold(I) complexes **10**, the corresponding Au(I) species was also generated. However, the proof on the generation of chelated NHC-oxazoline gold(I) complexes could not be observed. The ^1H NMR spectra of the catalytic species generated by combination of complex **10a** and Selectfluor only gave complex mixtures and could not detect any useful information. We assumed that the long distance between the NHC ligand and the oxazoline ligand probably led to the complex coordination mode of active species. This might explain the low catalytic activities of complexes **10** in the reaction.

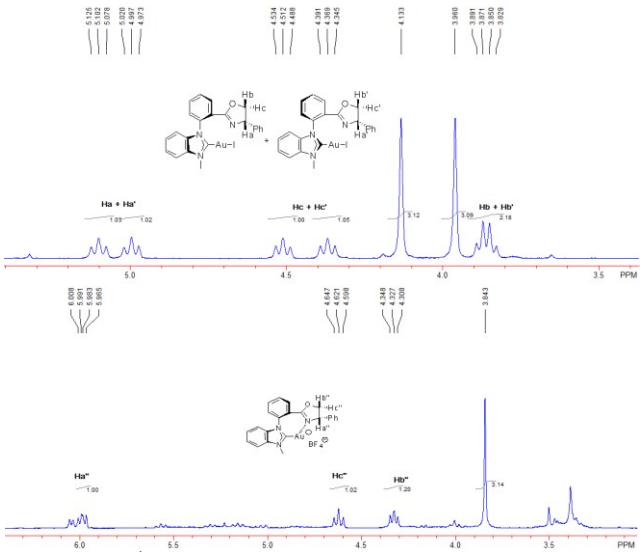
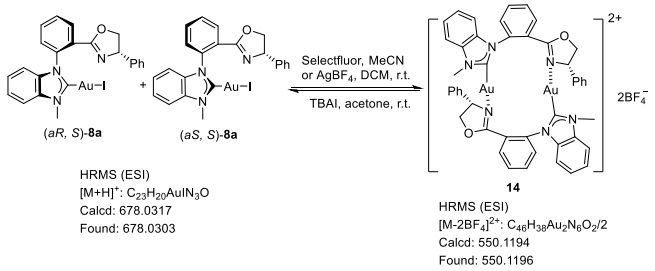


Figure 5. The ^1H NMR spectra of complex **8a** and complex **8a** after adding Selectfluor

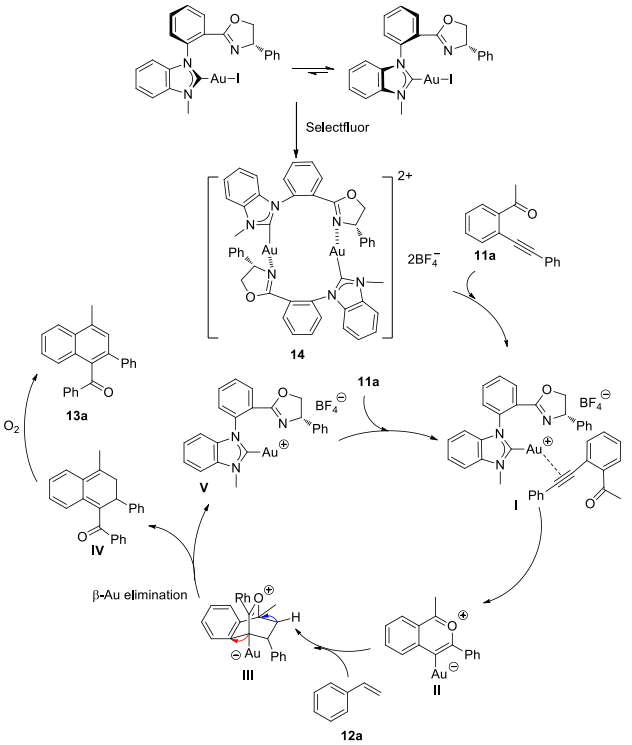
Some of control experiments were also carried out to verify our hypothesis (Scheme 4). The chelated NHC-oxazoline gold(I) complex **14** could be also synthesized through the common anion-exchange process. The NHC-gold(I) complex **8a** and 1.1 equivalent of $AgBF_4$ were stirred in dichloromethane at room temperature for 0.5 h. After that, the mixture was filtered through the celite pad twice to remove AgI and excess amount of $AgBF_4$ and to furnish the gold complex **14** with some inseparable impurities. The High ESI-Mass detection of gold complex **14** showed that the generated gold species' m/z was 550.1196 as a divalent species (z = 2), which indicated that the chelated NHC-oxazoline gold(I) complex **14** probably was formed as a binuclear structure. Consideration of the ESI-Mass result and the coordination mode of the gold(I) atom, we assumed that the complex **14** might be connected by two ligands and the gold(I) atoms end to end just like the coordination mode of Hoveyda group's bidentate NHC-oxygen Cu or Ag complexes.[18] The axial chirality of the complex **14** could not be identified at the present stage. The synthesized crude complex **14** generated from the complex **8a** and $AgBF_4$ was also used as the catalyst in the same reaction under the standard reaction conditions, furnishing the corresponding product **13a** in 90% yield. The bad performance of

the in situ generated gold(I) complex shown in Table 1, entry 4 might be attributed to the disturbance of the active silver(I) salt to this reaction.[19] Meanwhile, the combination of synthesized NHC-oxazoline gold(I) species **14** with two equivalents of tetrabutylammonium iodide (TBAI) in acetone at room temperature reversibly furnished the NHC-gold(I) complex **8a**, which was confirmed by its NMR and ESI-Mass spectra. All these experiments strongly supported our hypothesis.



Scheme 4. The controlled experiments

In Scheme 5, we proposed a plausible mechanism according to Zhu's previous work and our findings. Firstly, the diastereoisomer of complex (*aR*, *S*)-**8a** and (*aS*, *S*)-**8a** could be transformed to the chelated NHC-oxazoline gold(I) species **14**, the practical axial chirality of chelated Au(I) species could not be identified at the present stage. In this specific reaction system, the Selectfluor probably oxidized the iodine atom preferentially to generate the ionic NHC-oxazoline gold(I) complexes instead of oxidize the gold(I) species to gold(III) species. Then the Au(I) species could be coordinated by the triple bond of alkyne moiety along with the dissociation of gold(I) atom and the oxazoline group. The nucleophilic attack of carbonyl oxygen to the alkyne moiety then took place to form intermediate **II**. The intermediate **II** could undergo a Diels-Alder reaction with styrene to afford intermediate **III**. The ligated gold atom could be dissociated through a β-metal elimination process to give the cyclic *o*-quinodimethane **IV**. The product **13a** could be obtained after an aromatization process of intermediate **IV** in the presence of air atmosphere. The dissociative ionic gold species **V** could coordinate with another enynone molecule to complete the catalytic cycle.



Scheme 5. The plausible mechanism for gold-catalyzed cycloaddition/oxidation reaction

Conclusions

In summary, we have synthesized a series of new *ortho*- and *meta*-substituted NHC-oxazoline ligands based on phenyl scaffold in a six-step pathway. These ligands could be used to coordinate with Au(Me_2S)Cl by a simple deprotonation process in the presence of NaOAc. The *ortho*-substituted NHC-oxazoline gold(I) complexes have been shown as a pair of diastereoisomers due to the appearance of axial chirality. The *meta*-substituted NHC-oxazoline gold(I) complexes have been exhibited as a single structure. Both structures of the two kinds of NHC-oxazoline gold(I) complexes have been confirmed by X-ray diffraction analyses and the oxazoline group did not connect with the gold atom. These NHC-oxazoline gold(I) complexes could be combined with Selectfluor in situ to catalyze the cycloaddition/oxidation reaction of enynone with alkenes using air as oxidant to give the naphthalene derivatives in good to excellent yields. In this reaction, a novel function of the Selectfluor reagent in gold-catalyzed reactions was disclosed. The Selectfluor preferentially oxidized the iodine atom to give the ionic chelated binuclear NHC-oxazoline gold(I) complexes instead of oxidizing the gold(I) complexes to gold(III) complexes on the basis of the NMR spectra and Mass spectroscopic analysis of complex **14**. Some of controlled experiments were also carried out to verify our hypothesis. In any event, the role of selectfluor should be still largely an oxidant. More investigations on these highly active ionic chelated NHC-oxazoline gold(I) complexes are on-going in our laboratory.

Experimental

General

Dichloromethane and acetonitrile were freshly distilled from calcium hydride. Toluene was distilled from sodium (Na) under argon (Ar) atmosphere. Melting points were measured on a Yanagimoto micro melting apparatus and uncorrected. NMR spectra were recorded with a Varian Mercury *vx* or Bruker spectrometer at 400 MHz (^{1}H NMR), 100 or 125 MHz (^{13}C NMR) and 376 MHz (^{19}F NMR) in $CDCl_3$, respectively. Chemical shift were reported in ppm down field from internal TMS. Optical rotations were determined at 589 nm (sodium D line) using a Perkin Elmer 341 MC Polarimeter. $[\alpha]_D$ values are given with units of 10 cm^2 deg^{-1} g^{-1}. Mass spectra were recorded on the HP-5989 instrument by EI/ESI methods. Infrared spectra were recorded on a Perkin-Elmer PE-983 spectrometer with absorption in cm^{-1}. Satisfactory CHN microanalyses were obtained by using a Carlo-Erba 1106 analyzer. X-ray diffraction analysis was performed by using a Bruker Smart-1000 or Bruker SMART APEXIIX-ray diffractometer. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with Huanghai GF_{254} silica gel coated plates. Flash column chromatography was carried out using by using 300~400 mesh silica gel at increased pressure.

Synthesis of methyl 2-((2-nitrophenyl)amino) benzoate 2

Methyl anthranilate (0.3 g, 2.0 mmol), 1-bromo-2-nitrobenzene (0.45 g, 2.2 mmol), $Pd(OAc)_2$ (22.5 mg, 0.1 mmol), DPE-phos (108.0 mg, 0.2 mmol), and Cs_2CO_3 (0.98 g, 3.0 mmol) were stirred in anhydrous toluene (10 mL) at 80 ^{o}C under argon atmosphere for 16 h. The reaction mixture was cooled to room temperature, then 10 mL H_2O was added and stirred for 15 min. The mixture was extracted with DCM (3 x 20 mL) and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by a silica gel flash column chromatography (ethyl acetate/petroleum ether = 1/10) to afford the desired product **2**.

It is a known compound (0.54 g, 99%),[20] ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 11.14 (s, 1H), 8.17 (dd, *J* = 1.6, 8.4 Hz, 1H), 8.04 (dd, *J* = 1.6, 7.6 Hz, 1H), 7.62-7.60 (m, 1H), 7.52 (d, *J* = 7.6 Hz, 1H), 7.47-7.42 (m, 2H), 7.07-7.03 (m, 1H), 6.96-6.92 (m, 1H), 3.97 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.5, 142.3, 139.0, 137.3, 134.7, 133.4, 132.0, 126.6, 121.8, 119.9, 119.0, 118.6, 118.5, 52.3.

Synthesis of methyl 2-(2-aminophenylamino)-benzoate 3

A mixture of compound **2** (0.54 g, 2.0 mmol), 10% Pd-C (0.05 g) in a solution of MeOH (20 mL) were stirred for 3 h under reflux under 1 atm of H_2. After cooling to room temperature, Pd/C was removed by filtration. The resulting solution was evaporated to remove solvent under reduced pressure. The residue was purified by a silica gel flash column chromatography (ethyl acetate/petroleum ether = 1/8) to afford the desired product **3**.

It is a known compound (0.46 g, 95%),[20] ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.96 (s, 1H), 7.95 (dd, *J* = 1.6, 8.0 Hz, 1H), 7.28-7.24 (m, 1H), 7.14-7.06 (m, 2H), 6.82-6.75 (m, 2H), 6.70-6.61 (m, 2H), 3.91 (s, 3H), 3.81 (br, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 149.5, 143.3, 134.4, 131.4, 127.7, 127.1, 125.9, 118.8, 116.4, 115.9, 113.7, 110.9, 51.7.

Synthesis of methyl 2-(1*H*-benzo[*d*]imidazol-1-yl) benzoate 4

The compound **3** (0.73 g, 3.0 mmol) and triethyl orthoformate $[HC(OC_2H_5)_3]$ (8.0 mL) containing a catalytic amount of TsOH were heated at 100 ^{o}C for 16 h. After cooling to room temperature, ethyl acetate was added to form an azeotropic solution in order to remove the excess amount of triethyl orthoformate under reduced pressure. The residue was purified by a silica gel flash column chromatography (ethyl acetate/petroleum ether = 1/2) to afford the desired product **4**.

It is a known compound (0.64 g, 85%),[21] ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.11-8.09 (m, 1H), 8.00 (s, 1H), 7.87 (d, *J* = 7.2 Hz, 1H), 7.74-7.69 (m, 1H), 7.62-7.58 (m, 1H), 7.48 (d, *J* = 7.6 Hz, 1H), 7.33-7.25 (m, 2H), 7.16 (d, *J* = 7.6 Hz, 1H), 3.48 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 143.1, 135.1, 135.0, 133.2, 131.9, 129.0, 128.32, 128.28, 123.5, 122.4, 120.3, 109.7, 52.3.

Synthesis of compounds 5

A solution of amino alcohol (4.0 mmol), compound **4** (0.5 g, 2.0 mmol), Cs_2CO_3 (1.3 g, 4.0 mmol), and toluene (15 mL) was stirred at 80 ^{o}C for 24 h. After cooling to room temperature, the mixture was diluted with DCM, and washed with cold water, and brine. The organic layer was dried over anhydrous $MgSO_4$. After removal of the solvent in vacuo, the residue was purified by a silica gel flash column chromatography (petroleum ether/ethyl acetate, 1/1-0/1) to afford the desired product **5b.** But for the compound **5a**, it was hard to be dissolved in almost any solvent, so after the reaction was accomplished, the mixture was filtered, the residue was washed with toluene (3×10 mL) and water (60 mL) to remove the substrates and base. The pure product **5a** was used directly to the next step after dried in vacuo.

(*S*)-2-(1*H*-benzo[*d*]imidazol-1-yl)-*N*-(2-hydroxy-1-phenylethyl) benzamide (5a): It is a white solid (0.59 g, 83%). M.p. 205.1-206.3 ^{o}C. ^{1}H NMR (400 MHz, *d*-DMSO) δ 8.85 (d, *J* = 8.4 Hz, 1H), 8.26 (s, 1H), 7.76-7.57 (m, 6H), 7.31-7.28 (m, 5H), 7.11-7.09 (m, 2H), 4.86 (br, 1H), 4.75 (q, *J* = 7.2 Hz, 1H), 3.46-3.41 (m, 2H), 3.38 (br, 1H). ^{13}C NMR (100 MHz, *d*-DMSO) δ 166.1, 144.0, 143.2, 140.5, 134.6, 134.5, 133.0, 131.1, 129.3, 128.7, 128.1, 127.6, 126.9, 126.8, 123.1, 122.1, 119.6, 110.6, 64.4, 55.5. IR (KBr) ν 3755, 3276, 2935, 1644, 1577, 1560, 1499, 1289, 1238, 1066, 1033, 921, 911, 872, 745, 694, 668 cm^{-1}. MS (ESI) m/z: 358.2 (M^++H). HRMS (ESI) Calcd. for $C_{22}H_{20}N_3O_2$ requires: 358.1556. Found: 358.1549.

(*S*)-2-(1*H*-benzo[d]imidazol-1-yl)-*N*-(1-hydroxy-3-methylbutan-2-yl) benzamide (**5b**): It is a white solid (0.6 g, 92%). M.p. 156.3-157.8 ^{o}C. $[\alpha]^{20}_D$ -36.2 (*c* 0.75, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.05 (s, 1H), 7.83 (dd, *J* = 1.6, 7.6 Hz, 1H), 7.75-7.72 (m, 1H), 7.64-7.55 (m, 2H), 7.44-7.42 (m, 1H), 7.33-7.27 (m, 3H), 6.11 (d, *J* = 8.8 Hz, 1H), 3.65-3.59 (m, 1H), 3.33 (dd, *J* = 5.2, 10.8 Hz, 1H), 3.17 (dd, *J* = 3.6, 10.8 Hz, 1H), 2.92 (br, 1H), 1.64-1.52 (m, 1H), 0.67 (d, *J* = 6.8 Hz, 3H),

0.62 (d, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 143.2, 143.0, 134.6, 134.4, 132.5, 131.4, 130.0, 129.3, 127.5, 124.1, 123.1, 120.2, 110.3, 62.2, 56.9, 28.7, 19.0, 18.4. IR (KBr) ν 3302, 3079, 2959, 1643, 1606, 1588, 1542, 1496, 1458, 1367, 1296, 1233, 1209, 1164, 1053, 898, 811, 783, 742, 693 cm^{-1}. MS (ESI) m/z: 324.2 (M^++H). HRMS (ESI) Calcd. for $C_{19}H_{22}N_3O_2$ requires: 324.1712. Found: 324.1706.

Synthesis of compound 6

$SOCl_2$ (0.36 mL, 5.1 mol) was slowly added to a solution of compound **5** (1.0 mol) in 1,2-dichloroethane (10 mL) at 0 °C. The resulting solution was stirred at 40 °C for 5 h, and then the solvent was removed under reduced pressure. Subsequently, the residue was treated with sodium methoxide (0.43 g, 8.0 mol) in CH_3OH (15 mL), and stirred overnight under reflux. The resulting mixture was diluted with cold water, and extracted with DCM (3 x 20 mL). The organic layer was washed with brine, and dried over anhydrous Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by a silica gel flash column chromatography (ethyl acetate/petroleum ether = 2/1) to afford desired product **6**.

(*S*)-2-(2-(1*H*-benzo[*d*]imidazol-1-yl)phenyl)-4-phenyl-4,5-dihydrooxazole (**6a**): It is a colorless oil (0.26g, 78%). $[\alpha]^{20}_D$ -62.2 (*c* 1.15, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.13 (dd, J = 1.2, 7.6 Hz, 1H), 8.06 (s, 1H), 7.87 (d, J = 7.2 Hz, 1H), 7.71-7.67 (m, 1H), 7.62-7.58 (m, 1H), 7.51 (dd, J = 1.2, 7.6 Hz, 1H), 7.34-7.19 (m, 6H), 6.95-6.93 (m, 1H), 5.12 (t, J = 10.0 Hz, 1H), 4.33 (t, J = 8.8 Hz, 1H), 3.75 (t, J = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.9, 143.34, 143.3, 141.3, 135.1, 134.9, 132.2, 131.7, 129.1, 128.6, 128.2, 127.5, 126.5, 126.0, 123.5, 122.4, 120.4, 110.1, 74.9, 69.7. IR (KBr) ν 2959, 2928, 1652, 1615, 1601, 1502, 1460, 1352, 1308, 1289, 1261, 1230, 1106, 1078, 1062, 1036, 955, 890, 788, 765, 743, 688 cm^{-1}. MS (ESI) m/z: 340.1 (M^++H). HRMS (ESI) Calcd. for $C_{22}H_{18}N_3O$ requires: 340.1450. Found: 340.1444.

(*S*)-2-(2-(1*H*-benzo[*d*]imidazol-1-yl)phenyl)-4-isopropyl-4,5-dihydrooxazole (**6b**): It is a colorless oil (0.25 g, 81%). $[\alpha]^{20}_D$ -66.1 (*c* 0.82, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.04-8.01 (m, 2H), 7.85 (d, J = 8.0 Hz, 1H), 7.67-7.63 (m, 1H), 7.59-7.55 (m, 1H), 7.49 (d, J = 7.6 Hz, 1H), 7.31-7.18 (m, 3H), 3.96 (t, J = 8.4 Hz, 1H), 3.82-3.76 (m, 1H), 3.65 (t, J = 8.4 Hz, 1H), 1.51-1.43 (m, 1H), 0.76-0.71 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.3, 143.3, 143.2, 134.9, 134.7, 131.8, 131.4, 128.9, 127.9, 126.2, 123.3, 122.3, 120.1, 110.0, 72.5, 70.6, 32.6, 18.5, 18.2. IR (KBr) ν 2960, 2922, 1648, 1614, 1602, 1502, 1460, 1356, 1310, 1287, 1261, 1231, 1205, 1107, 1079, 1062, 1034, 1008, 950, 788, 764, 745, 700 cm^{-1}. MS (ESI) m/z: 306.2 (M^++H). HRMS (ESI) Calcd. for $C_{19}H_{20}N_3O$ requires: 306.1606. Found: 306.1601.

Synthesis of compound 7

Compound **6** (0.4 mmol) and MeI (0.25 mL, 4.0 mmol) in MeCN (10 mL) were stirred under reflux until the substrate disappeared. After cooling to room temperature, volatiles were removed under reduced pressure and the obtained solid compound **7** was used for the next reaction without any further purification.

Synthesis of *orthor* NHC-oxazaoline gold(I) complex 8

Compound **7** (0.4 mmol), NaOAc (66 mg, 0.8 mmol) and $Au(Me_2S)Cl$ (118 mg, 0.4 mmol) were added to a dry flask under argon, then refluxed in MeCN (20 mL) for 2 days. The volatiles were removed under reduced pressure and the residue was purified by a silica gel flash column chromatography (eluent: petroleum ether/EtOAc = 2:1) to give the product **8**.

Complex 8a [The ratio of (*aR*, *S*)-**8a** and (*aS*, *S*)-**8a** is 1:1]: It is a white solid (199 mg, 85%). M.p. 210.2-212.0 °C. $[\alpha]^{20}_D$ -29.3 (*c* 0.75, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.20 (t, J = 8.4 Hz, 2H), 7.74-7.59 (m, 6H), 7.48-7.29 (m, 9H), 7.15-7.09 (m, 7H), 6.64 (d, J = 6.0 Hz, 2H), 5.08 (t, J = 9.2 Hz, 1H), 4.98 (t, J = 9.2 Hz, 1H), 4.49 (t, J = 8.8 Hz, 1H), 4.35 (t, J = 8.8 Hz, 1H), 4.11 (s, 3H), 3.94 (s, 3H), 3.86 (d, J = 8.0, 1H), 3.82 (d, J = 8.4, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.9 (188.8), 161.5 (161.2), 141.6 (141.3), 135.5 (134.9), 133.2 (133.0), 132.6 (132.5), 132.4, 131.7 (131.5), 130.3 (130.2), 129.7 (129.2), 128.6 (128.4), 127.5 (127.2), 126.9 (126.2), 126.1 (125.7), 124.8 (124.5), 111.9 (111.8), 111.2 (111.0), 74.0 (73.99), 70.2 (69.9), 34.9 (34.6). IR (KBr) ν 2924, 2853, 1644, 1601, 1504, 1455, 1387, 1358, 1311, 1263, 1243, 1204, 1096, 1057, 1035, 954, 895, 787, 699, 661 cm^{-1}. MS (ESI) m/z: 678.0 (M^++H). HRMS (ESI) Calcd. for $C_{23}H_{20}N_3OAuI$ requires: 678.0317. Found: 678.0303.

Complex 8b [The ratio of (*aR*, *S*)-**8b** and (*aS*, *S*)-**8b** is 1:1.2]: It is a yellow solid (201 mg, 91%). M.p. 156.0-157.6 °C. $[\alpha]^{20}_D$ -58.1 (*c* 0.33, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.10 (d, J = 7.2 Hz, 1.83H), 7.71-7.42 (m, 9.2H), 7.39-7.31 (m, 1.83H), 7.11 (d, J = 8.0 Hz, 1H), 7.03 (d, J = 8.0 Hz, 0.83H), 4.15-4.12 (m, 6.5H), 3.92 (t, J = 8.8 Hz, 0.83H), 3.75-3.58 (m, 3.8H), 1.58-1.51 (m, 1H), 1.19-1.12 (m, 0.85H), 0.69 (d, J = 6.8 Hz, 6H), 0.57 (d, J = 6.8 Hz, 2.5H), 0.44 (d, J = 6.8 Hz, 2.5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.6 (188.4), 160.0 (159.5), 135.3 (135.2), 134.8 (134.7), 133.1 (132.9), 132.1 (131.9), 131.3 (131.1), 130.1 (129.5), 129.1, 126.4 (125.8), 124.8 (124.6), 124.5 (124.4), 111.9 (111.8), 110.94 (110.89), 73.1 (72.7), 70.3 (69.9), 34.9 (34.8), 32.9 (32.7), 18.74 (18.67), 18.5 (18.1). IR (KBr) ν 2960, 2924, 1651, 1453, 1391, 1261, 1102, 1022, 1009, 913, 801, 752, 670 cm^{-1}. MS (ESI) m/z: 644.0 (M^++H). HRMS (ESI) Calcd. for $C_{20}H_{22}N_3OAuI$ requires: 644.0473. Found: 644.0460.

Synthesis of meta NHC-oxazoline gold(I) complex 10

Compound **9** (0.2 mmol), NaOAc (33 mg, 0.4 mmol) and $Au(Me_2S)Cl$ (59 mg, 0.2 mmol) were added to a dry flask under argon, then refluxed in MeCN (10 mL) for 2 days. The volatiles were removed under reduced pressure and the residue was purified by a silica gel flash column chromatography (eluent: petroleum ether/EtOAc = 2:1) to give the product **10**.

Complex 10a: It is a white solid (88.0 mg, 75% yield). M.p. 152.1-153.3 °C. $[\alpha]^{20}_D$ -11.3 (*c* 0.80, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.28 (s, 1H), 8.24 (d, J = 7.6 Hz, 1H), 7.86 (d, J = 8.0 Hz, 1H), 7.70 (t, J = 8.0 Hz, 1H), 7.57-7.30 (m, 9H), 5.43 (t, J = 8.8 Hz, 1H), 4.85 (t, J = 8.4 Hz, 1H), 4.33 (t, J = 8.0 Hz, 1H), 4.18 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.8, 163.3, 141.9, 136.9, 133.6, 133.4, 130.2, 129.6, 129.5, 128.8, 127.7, 126.7, 126.3, 125.3, 125.2, 112.2, 111.4, 75.2, 70.2, 35.1.

IR (KBr) ν 2955, 2924, 1657, 1593, 1583, 1494, 1456, 1390, 1354, 1260, 1092, 1023, 796, 743 cm^{-1}. MS (ESI) m/z: 903.3 (2NHC+Au^+). HRMS (ESI) Calcd. for $C_{46}H_{38}N_6O_2Au$ requires: 903.2722. Found: 903.2727.

Complex 10b: It is a yellow solid (92.8 mg, 82%). M.p. 183.2-183.9 °C. $[\alpha]^{20}_D$ -13.9 (*c* 0.30, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 8.17-8.14 (m, 2H), 7.80 (d, *J* =8.0 Hz, 1H), 7.65 (t, *J* = 8.0 Hz, 1H), 7.57-7.39 (m, 4H), 4.39 (t, *J* = 8.8 Hz, 1H), 4.27 (t, *J* = 8.0 Hz, 1H), 4.18 (s, 3H), 4.08 (dd, *J* = 8.0, 10.0 Hz, 1H), 0.96 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.9, 161.8, 136.7, 133.7, 133.4, 130.1, 130.0, 129.4, 129.3, 126.1, 125.3, 125.2, 112.3, 111.4, 76.4, 69.1, 35.0, 34.0, 25.9. IR (KBr) ν 2953, 2926, 2866, 1727, 1652, 1602, 1585, 1477, 1456, 1392, 1363, 1309, 1260, 1237, 1201, 1101, 1086, 1057, 1027, 980, 954, 906, 837, 821, 797, 748, 706, 695, 662 cm^{-1}. MS (ESI) m/z: 863.3 (2NHC+Au^+). HRMS (ESI) Calcd. for $C_{42}H_{46}N_6O_2Au$ requires: 863.3348. Found: 863.3352.

Complex 10c: It is a yellow solid (57.0 mg, 46%). M.p. 147.2-149.0 °C. $[\alpha]^{20}_D$ -13.6 (*c* 0.55, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 8.28 (s, 1H), 8.23 (d, *J* = 7.6 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.73-7.67 (m, 2H), 7.49-7.47 (m, 8H),5.61 (q, *J* = 6.8 Hz, 1H), 5.43 (t, *J* = 8.8 Hz, 1H), 4.85 (dd, *J* = 8.8, 10.0 Hz, 1H), 4.32 (t, *J* = 8.4 Hz, 1H), 1.82 (d, *J* = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.4, 163.3, 141.9, 137.0, 134.5, 131.3, 130.2, 129.8, 129.5, 129.4, 128.8, 127.7, 126.8, 126.6, 125.0, 124.8, 112.9, 112.6, 75.2, 70.2, 54.0, 21.8. IR (KBr) ν 2958, 2927, 1652, 1615, 1602, 1502, 1460, 1353, 1308, 1289, 1261, 1230, 1204, 1107, 1078, 1062, 1033, 1009, 958, 788, 764, 743 cm^{-1}. MS (ESI) m/z: 706.1 (M^++H). HRMS (ESI) Calcd. for $C_{25}H_{24}N_3OAuI$ requires: 706.0630. Found: 706.0615.

Typical Selectfluor promoted NHC-oxazoline gold(I) complexes catalyzed cycloaddition/oxidation reaction

The corresponding enynones (0.1 mmol) and styrene (0.5 mmol) were added to a solution of the catalyst combination of NHC-oxazoline gold(I) complex (5 mol%) and Selectfluor (15 mol%) in DCE (2 mL, 0.05 M). The reaction mixture was stirred under an air atmosphere at 80 °C until the substrate disappeared. After the reaction was finished, the mixture was filtered by a short silica, and then the solvent was evaporated under reduced pressure and the residue was purified by flash chromatography on silica gel to afford the desired products **13**.

Compound 13a: It is a known compound (29.7 mg, 92%).[17] ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 8.10 (d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 8.4 Hz, 1H), 7.63-7.61 (m, 2H), 7.56 (dt, *J* = 1.6, 6.8 Hz, 1H), 7.46 (dt, *J* = 1.2, 6.8 Hz, 1H), 7.43 (s, 1H), 7.40-7.32 (m, 3H), 7.24-7.18 (m, 4H), 7.18-7.14 (m, 1H), 2.81 (d, *J* = 0.4 Hz, 3H).

Compound 13b: It is a colorless oil (31.9 mg, 95%). ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 8.07 (d, *J* = 8.4 Hz, 1H), 7.71 (d, *J* = 8.4 Hz, 1H), 7.63 (d, *J* = 8.8 Hz, 2H), 7.53 (dt, *J* = 1.2, 7.2 Hz, 1H), 7.45-7.35 (m, 3H), 7.24-7.22 (m, 4H), 7.01 (d, *J* = 8.0 Hz, 2H), 2.78 (s, 3H), 2.23 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.0, 138.1, 137.4, 137.0, 136.99, 135.9, 133.9, 133.1, 131.5, 130.8, 129.6, 129.2, 128.9, 128.5, 128.2, 126.7, 126.1, 126.0, 124.2, 21.0, 19.6. IR (KBr) ν 2921, 1663, 1596, 1579, 1508, 1448, 1370, 1312, 1250, 1225, 1175, 1072, 1051, 1023, 989, 894, 872, 791, 736, 711 cm^{-1}. MS (ESI) m/z: 337.2 ($M+H^+$). HRMS (ESI) Calcd. for $C_{25}H_{21}O$ requires: 337.1592. Found: 337.1583.

Compound 13c: It is a colorless solidified oil (19.1 mg, 57%). ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 8.13 (d, *J* = 8.4 Hz, 1H), 7.95 (d, *J* = 7.6 Hz, 2H), 7.62 (d, *J* = 8.4 Hz, 1H), 7.59-7.56 (m, 2H), 7.51 (d, *J* = 7.2 Hz, 1H), 7.43-7.37 (m, 4H), 7.28 (d, *J* = 7.2 Hz, 1H), 7.15 (t, *J* = 7.6 Hz, 1H), 4.10 (s, 2H), 2.82 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.4, 144.0, 139.6, 139.1, 137.5, 135.9, 134.0, 131.5, 130.5, 130.4, 129.9, 128.9, 128.6, 127.6, 126.9, 125.9, 125.7, 125.6, 125.1, 123.9, 123.4, 36.0, 15.5. IR (KBr) ν 2922, 2852, 1665, 1595, 1580, 1509, 1466, 1448, 1411, 1380, 1317, 1296, 1284, 1232, 1191, 1172, 1098, 1023, 890, 864, 779, 762, 737, 725 cm^{-1}. HRMS (EI) Calcd. for $C_{25}H_{18}O$ requires: 334.1358. Found: 334.1360.

Compound 13d: It is a colorless oil (19.7 mg, 65%). ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 8.07-8.05 (m, 1H), 7.83-7.81 (m, 1H), 7.58-7.52 (m, 2H), 7.44-7.37 (m, 6H), 2.76 (d, *J* = 0.8 Hz, 3H), 2.26 (t, *J* = 7.2 Hz, 2H), 1.45-1.38 (m, 2H), 1.11-1.02 (m, 2H), 0.69 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.2, 142.6, 140.5, 136.9, 135.8, 135.6, 131.7, 129.4, 128.6, 128.2, 127.8, 126.9, 126.1, 125.4, 124.3, 45.0, 25.8, 22.0, 19.6, 13.6. IR (KBr) ν 2957, 2928, 2870, 1695, 1596, 1508, 1449, 1405, 1376, 1176, 1073, 1031, 881, 758, 702, 669 cm^{-1}. HRMS (EI) Calcd. for $C_{22}H_{22}O$ requires: 302.1671. Found: 302.1672.

Compound 13e: It is a yellow oil (20.6 mg, 72%). ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 8.07-8.05 (m, 1H), 7.92-7.90 (m, 1H), 7.58-7.53 (m, 2H), 7.48-7.37 (m, 6H), 2.76 (d, *J* = 0.8 Hz, 3H), 1.88-1.82 (m, 1H), 1.12-1.09 (m, 2H), 0.71-0.66 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.3, 140.8, 137.3, 136.4, 136.0, 131.7, 129.6, 129.4, 128.3, 127.6, 126.9, 126.1, 125.9, 124.2, 24.8, 20.0, 13.0. IR (KBr) ν 2955, 2922, 2851, 1695, 1596, 1508, 1497, 1444, 1406, 1376, 1352, 1308, 1262, 1193, 1177, 1140, 1076, 1030, 943, 882, 864, 789, 762, 703, 666 cm^{-1}. HRMS (EI) Calcd. for $C_{21}H_{18}O$ requires: 286.1358. Found: 286.1360.

Compound 13f: It is a known compound (9.9 mg, 32%).[17] ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 8.01 (d, *J* = 8.4 Hz, 1H), 7.94 (d, *J* = 8.4 Hz, 1H), 7.73 (d, *J* = 8.4 Hz, 1H), 7.61 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 1H), 7.52 (t, *J* = 7.2 Hz, 1H), 7.45 (t, *J* = 7.2 Hz, 1H), 7.40-7.34 (m, 3H), 7.23-7.20 (m, 4H), 7.18-7.16 (m, 1H).

Compound 13g: It is a colorless solidified oil (27.9 mg, 70%). ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 8.00-7.98 (m, 1H), 7.77-7.75 (m, 1H), 7.63-7.58 (m, 4H), 7.55-7.51 (m, 3H), 7.49-7.39 (m, 5H), 7.23-7.16 (m, 3H), 7.07 (d, *J* = 8.0 Hz, 2H), 2.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.4, 144.3, 141.6, 140.14, 140.12, 136.6, 135.5, 135.3, 131.2, 130.7, 130.1, 129.8, 129.4, 129.1, 128.7, 128.4, 128.2, 127.6, 127.4, 126.9, 126.3, 126.27, 126.0, 21.7. IR (KBr) ν 2923, 2852, 1665, 1604, 1573, 1508, 1493, 1445, 1407, 1366, 1309, 1259, 1230, 1179, 1150, 1075, 1051, 1032, 949, 894, 789, 758, 728, 701, 668 cm^{-1}. MS (ESI) m/z: 399.2

($M+H^+$). HRMS (ESI) Calcd. for $C_{30}H_{23}O$ requires: 399.1749. Found: 399.1741.

Acknowledgements

We thank the Shanghai Municipal Committee of Science and Technology (11JC1402600), the National Basic Research Program of China (973)-2015CB856603, and the National Natural Science Foundation of China (20472096, 21372241, 21361140350, 20672127, 21421091, 21372250, 21372075, 21121062, 21302203 and 20732008).

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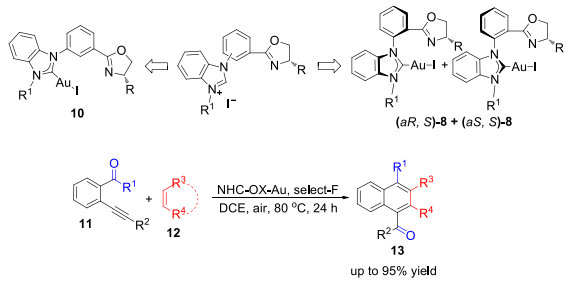
22

Selectfluor promoted NHC-Oxazoline gold(I) complexes catalyzed cycloaddition/oxidation reaction of enynones with alkenes



The two kinds of *ortho*- and *meta*-oxazoline substituted NHC-gold(I) complexes have been synthesized. These gold complexes could react with Selectfluor to give ionic chelated NHC-oxazoline gold(I) complexes which could smoothly catalyze the cycloaddition/oxidation reaction of enynones with alkene to afford the corresponding naphthalene derivatives with moderate to excellent yields.

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