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J. Org. Chem., **Just Accepted Manuscript** • DOI: 10.1021/acs.joc.6b01948 • Publication Date (Web): 28 Aug 2016

Just Accepted

ACS Publications

The Journal of Organic Chemistry is published by the American Chemical Society.
1155 Sixteenth Street N.W., Washington, DC 20036

Gold-Catalyzed β-Regioselective Formal [3+2] Cycloaddition of Ynamides with Pyrido[1,2-b]indazoles: Reaction Development and Mechanistic Insights

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Keywords

Gold catalysis, ynamides, pyrido[1,2-b]indazoles, β-site regioselectivity, 3-aminoindole

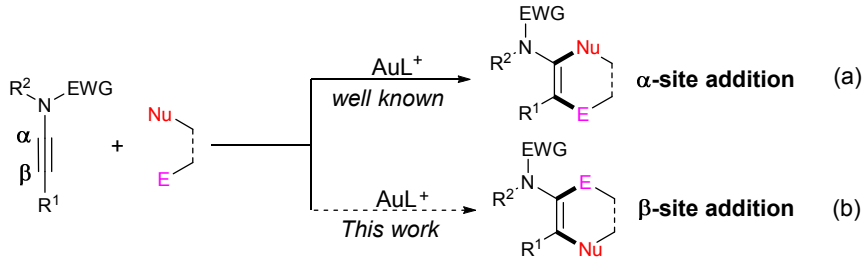
Abstract

Here we report an unprecedented gold(I) induced β-site regioselective formal [3+2] cycloaddition of ynamides with pyrido[1,2-b]indazoles, giving 3-amido-7-(pyrid-2'-yl)indoles in good to excellent yields. A complex of gold(I)-catalyst with ynamide was isolated and characterized by X-ray diffraction analysis for the first time. Mechanistic investigations suggest

the reaction pathway involves a gold-stabilized carbocation intermediate, which in turn participated in sequential C-H bond functionalization of the *ortho*-position of the phenyl ring.

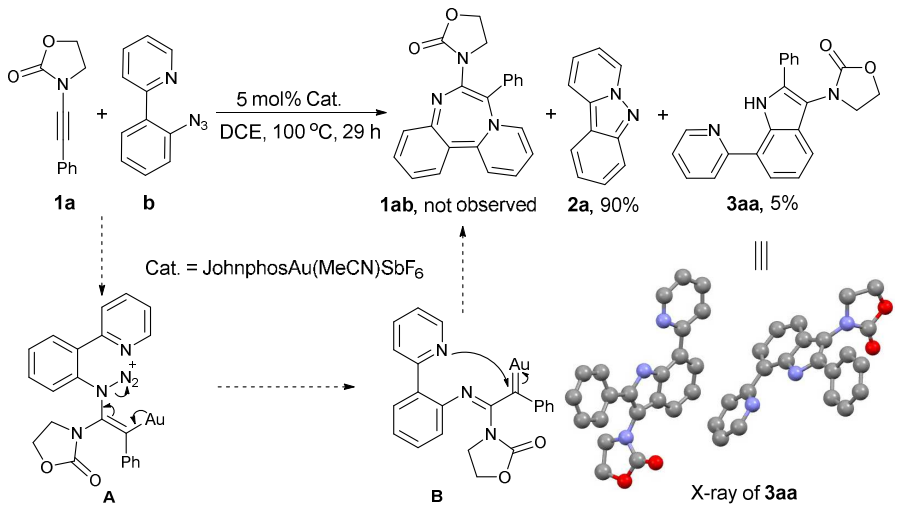
Introduction

Ynamides are bench stable and easily accessible starting materials. In the past decade, a large library of nitrogen-containing molecules have been prepared via addition of nucleophiles to the α-site of ynamides (Scheme 1a).[1,2] In contrast, the addition of nucleophiles at the β position of the triple bond is comparatively less common.[3,4] Very recently, Marek,[3a] Lam[3c] and others[3d,3e] reported carbometallation of ynamides in presence of proper copper(I) or rhodium(I) salts, in which the tethered carbomate functionality was crucial for the β-regioselectivity by acting as a chelating group. Herein, we report the first gold-catalyzed β-regioselective cycloaddition of ynamides with external reagents, giving 3-amidoindole derivatives in atom-economical manner (Scheme 1b). Hashmi[4a] and Gagosz[4b] have reported gold-catalyzed intramolecular cyclization of N-alkynyl tert-butyloxycarbomates independently. However, to our knowledge, gold-catalyzed intermolecular cycloaddition of ynamides with other reactants features β-regioselectivity has remained elusive to date.



Scheme 1. Gold-catalyzed formal cycloaddition of ynamides.

Gold-catalyzed reactions of alkynes with nucleophiles have received considerable attention.[5] Compared with the relatively well investigated approach to generate α-carbonyl gold-carbene,[6] similar but equally appealing concept on gold-catalyzed formation of α-imino carbene remains underdeveloped.[7] Seminal works on gold-catalyzed nitrene transfer by intramolecular reaction of alkynyl azides were first described by Toste in 2005,[8] and further demonstrated by Zhang,[9] Gagosz[10] and others.[11] Instead of azides, also anthranils and other nitrene-transfer reagents have been used as nitrene precursors.[12] Intermolecular reactions of azides with ynamides have also been realized by Ye,[13] Liu[14] and our group[15a-b] very recently. In conjunction with our continuing interest in nitrogen-containing molecules synthesis via α-imino carbene intermediates,[15] we envisioned that gold-catalyzed reaction of ynamide **1a** with azide **b** might generate intermediate **B**, which in turn undergo intramolecular cyclization with tethered pyridinyl moiety, thus eventually leading to the formation of fused tricyclic compound **1ab** (Scheme 2).



Scheme 2. Initial attempts towards original hypothesis.

Herein, we would like to present our detailed studies towards this goal, and disclose an unprecedented gold-catalyzed annulation of ynamides with pyrido[1,2-b]indazoles, providing 3-

amino-7-(pyrid-2'-yl)indoles in good to excellent yields. The regioselectivity of the current transformation suggests an unusual β-site cycloaddition of ynamide was involved. A series of mechanistic studies were performed to get valuable information on the reaction pathways. Moreover, a complex of gold catalyst with ynamide was isolated for the first time and characterized by single-crystal X-ray analysis.

Results and discussion

Optimization studies and substrate scope

To test our hypothesis, the reaction of ynamide **1a** and 2-(2-azidophenyl)pyridine **b** was evaluated initially (Scheme 2). Using JohnphosAu(MeCN)SbF_6 (Echavarren's catalyst, 5 mol%) as catalyst,[16] azide **b** was completely consumed after heating at 100 ^{o}C for 29 h in DCE (1,2-dichloroethane), while most ynamide **1a** remained intact, and the suspecting product **1ab** was not observed from the reaction mixture. Pyrido[1,2-b]indazole **2a** was obtained as the major product, which was presumably resulting from the ring closure of **b** by thermolysis.[17] Surprisingly, a new compound which was identified to be 3-amino-7-(pyrid-2'-yl)indole **3aa**[18] was obtained in 5% yield upon isolation. Unambiguous proof of structure and regioselectivity was achieved by single-crystal X-ray analysis. Pleasingly, under otherwise identical conditions, replacing **b** with pyrido[1,2-b]indazole **2a**, **3aa** was obtained as the sole product in nearly quantitative yield. It is worthwhile to mention that Hashmi[12a] and Ye[12c] reported elegant gold-catalyzed annulations of anthranils or isoxazoles with ynamides to synthesize polysubstituted pyrroles or 7-acylindoles very recently. In their report, α-site regiocontrolled addition of ynamides occurred exclusively. In contrast, the precise structure of **3aa** suggests an unusual β-site addition of ynamide **1a** take

place here. This observation indicates that a key reaction intermediate distinct from well accepted ketenimium ion was involved in this novel transformation (vide infra).

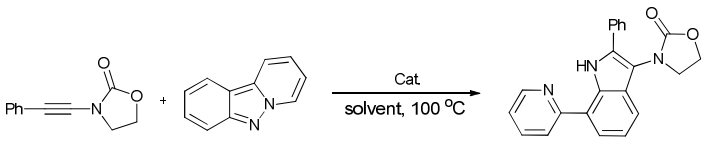
As one of the most important class of heterocycles, indole scaffolds are embedded in a wide range of natural products and pharmaceuticals.[19] Therefore, the development of efficient methodologies to access these compounds have received long term attention.[20] Compared with normal indole moiety, the classic Fisher cyclization is not applicable to prepare 7-(pyrid-2'-yl)indoles.[21] Moreover, regarding their potential utilities in pharmaceuticals and material science,[21b,22,23] and the abnormal β-regioselective addition of the ynamides in current transformation, we decided to explore the reaction of ynamides with pyrido[1,2-b]indazole systematically.

As depicted in Table 1, a series of gold catalysts containing different counter anions and ligands were examined. JohnphosAuNTf$_2$ was found to be less reactive (entry 2). Other cationic catalysts bearing simple phosphine or N-heterocycliccarbene ligands including PPh$_3$AuNTf$_2$, IAdAu(PhCN)SbF$_6$ and IPrAuNTf$_2$ were proved to be less efficient or totally inactive (entries 4-8). AgSbF$_6$ or HOTf showed no catalytic activity for the reaction (entries 9 and 10). The effects of solvent were also examined (entries 11-15). CH_2Cl_2, toluene and $CHCl_3$ were proper reaction media, while low yields of indole 3aa were observed when the reactions were performed in $MeNO_2$ or MeCN.

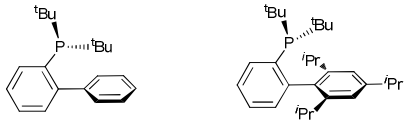
With a set of efficient reaction condition established (Table 1, entry 1), the reaction scope was explored by using pyrido[1,2-b]indazole **2a** as the nitrene precursor. Results are shown in Table 2. In general, both electron-donating (methyl, ethyl and methoxyl, cf. **3ba-3da**) and electron-withdrawing groups (Fluoro, chloro and bromo, cf. **3ea-3ia**) on the phenyl ring of ynamides **1**

were tolerated, furnishing the corresponding indoles in good to excellent yields. Moreover, ynamides bearing 1-naphthyl or 2-naphthyl at the terminal position of the triple bond were viable substrates. **3ja** and **3ka** were obtained in 99% and 82% yield, respectively. Ynamide (**1l**) derived from hex-1-yne, could participate in the reaction, albeit with 42% yield (cf. **3la**). The reaction of ynamide 1m bearing a chiral auxiliary group proceeded well, furnishing indole **3ma** in 76% yield. Given the abundance and the easy accessibility of chiral oxazolidin-2-ones, such kind of 7-(pyrid-2'-yl)indoles may have synthetic potential in the research area of chiral bidentated anion ligands.

Table 1. Optimization of the reaction conditions.[a]



1a **2a** **3aa**



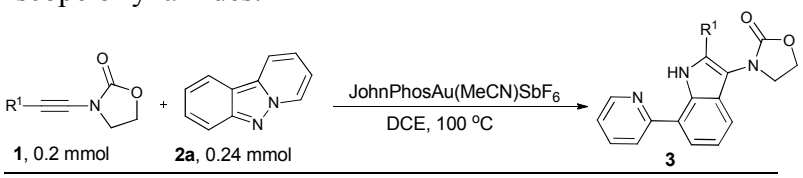
Johnphos ^{t}BuXphos

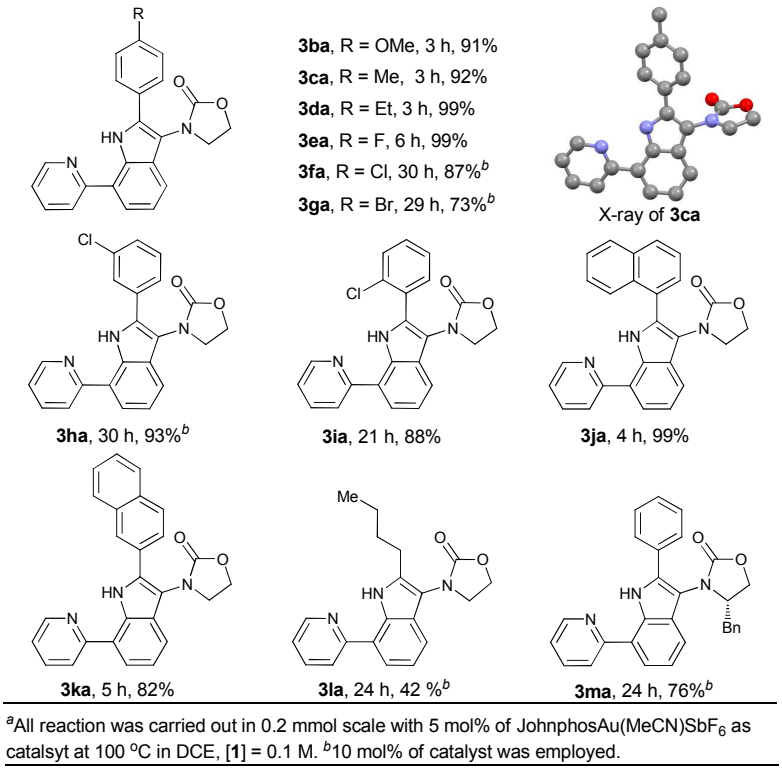
IAd: R = 1-adamantyl
IPr: R = 2,6-(^{i}Pr)$_2$C$_6$H$_3$
IMes: R = 2,4,6-(Me)$_3$C$_6$H$_2$

Entry	cat.	solvent	time (h)	yield (%)[b]
1	JohnPhosAu(MeCN)SbF$_6$	DCE	11	96 (95)[c]
2	JohnPhosAuNTf$_2$	DCE	16	88
3	JohnPhosAuCl	DCE	16	–
4	PPh$_3$AuNTf$_2$	DCE	16	31
5	^{t}BuXPhosAu(MeCN)SbF$_6$	DCE	22	8
6	IAdAu(PhCN)SbF$_6$	DCE	16	12
7	IPrAuNTf$_2$	DCE	16	–
8	IMesAuSbF$_6$	DCE	16	–
9	AgSbF$_6$	DCE	16	–
10	HOTf	DCE	16	–
11	JohnPhosAu(MeCN)SbF$_6$	DCM	16	85
12	JohnPhosAu(MeCN)SbF$_6$	Toluene	16	86
13	JohnPhosAu(MeCN)SbF$_6$	CHCl$_3$	16	83
14	JohnPhosAu(MeCN)SbF$_6$	MeNO$_2$	16	66
15	JohnPhosAu(MeCN)SbF$_6$	MeCN	16	71

[a] **1a** (0.2 mmol), **2a** (0.24 mmol) and 5 mol% of catalysts were stirred in solvent (1 mL) at 100 °C for proper reaction time. [b] Determined by ^{1}H NMR using CH_2Br_2 as internal standard. [c] Yield given within the parentheses refers to the pure product.

Table 2. Reaction scope of ynamides.[a]

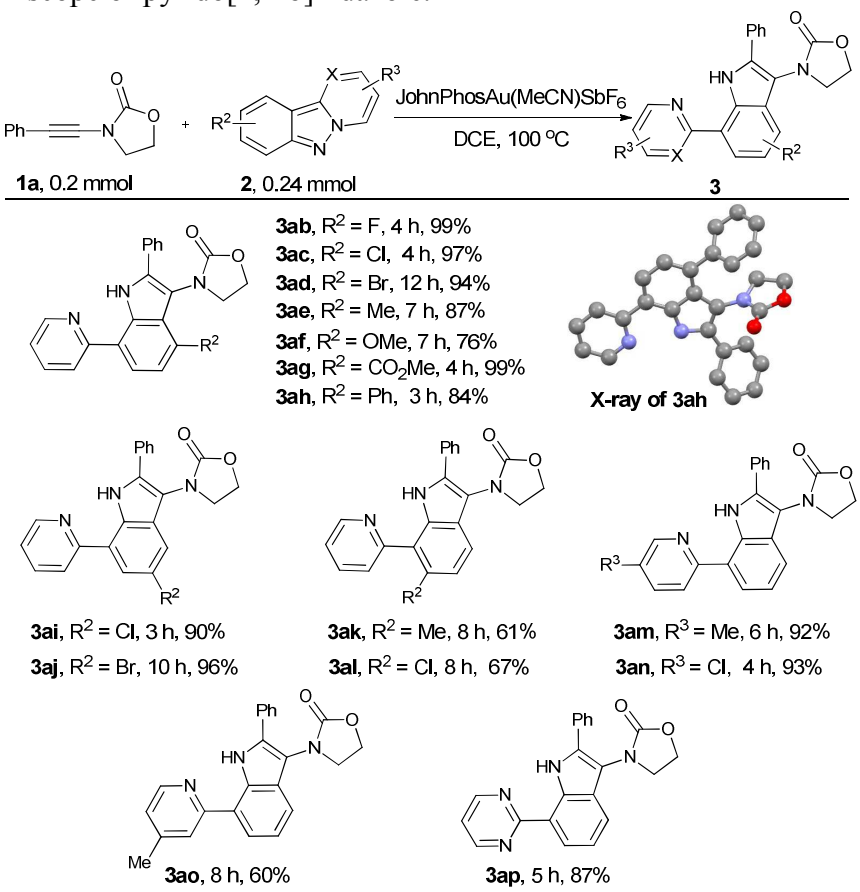




[a]All reaction was carried out in 0.2 mmol scale with 5 mol% of JohnphosAu(MeCN)SbF_6 as catalsyt at 100 °C in DCE, [**1**] = 0.1 M. [b]10 mol% of catalyst was employed.

Subsequently, the generality and limitation of pyrido[1,2-b]indazoles for the reaction with ynamide **1a** was investigated under the standard reaction condition. As depicted in Table 3, a broad set of substituents on pyrido[1,2-b]indazole were proved to be compatible (**3ab-3ap**). Notably, electron-withdrawing groups (R^2) trended to speed up the reaction and afford the corresponding products in higher yields (Table 3 and Scheme S1 in Supporting Information).

Table 3. Reaction scope of pyrido[1,2-b]indazole.[a]



[a]All reaction was carried out in 0.2 mmol scale with 5 mol% of JohnphosAu(MeCN)SbF_6 as catalyst at 100 °C in DCE, [**1a**] = 0.1 M.

Mechanistic studies

Detection and Characterization of Reaction Intermediates

The unusual regioselectivity of gold-catalyzed annulation between ynamides and pyrido[1,2-b]indazoles is intriguing. To get deeper understanding on the reaction mechanism, a series of experiments were subsequently conducted. The stoichiometric reactions of **1a** and **2a** with catalyst JohnphosAu(MeCN)SbF_6 were monitored by ^{31}P NMR spectroscopy in $CDCl_3$ at room temperature (Figure 1 and Figure S1 in Supporting Information). Treatment of **1a** with

JohnphosAu(MeCN)SbF_6 generated a new species with ^{31}P NMR shift at 64.28 ppm (Figure 1c), which has been identified to be the adduct of **1a** with the cationic gold catalyst. The structure of this complex was confirmed by X-ray crystallography,[24] which contained a fused bicyclic five-membered-ring system (Figure 2). Compared with the extensive studies on gold-catalyzed formal cycloaddition of ynamides in recent years, current outcome is noteworthy. As the well accepted keteniminium ion intermediate which would commonly lead to α-site selective cycloaddition product was not observed. More importantly, in previous reports, the activation mode of gold-catalyst with ynamide is somewhat speculative. No direct evidences for the actual reaction intermediate have been described. The adduct obtained here represents the first isolated gold complex with ynamide, and it well explained the unusual β-site regioselective addition observed in current transformation. Encouraged by this discovery, further systematical examinations on the complexation of gold catalysts with other ynamides will be the subject of our future studies.

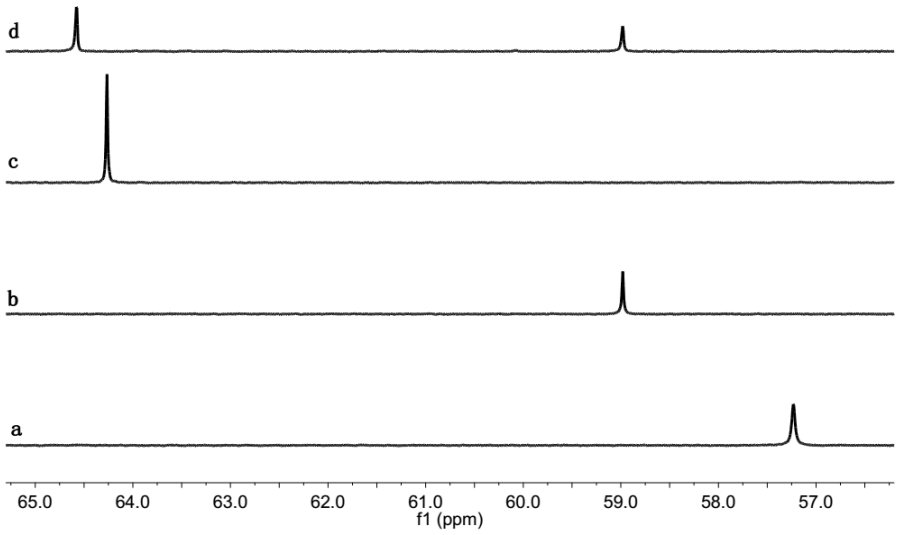


Figure 1. The ^{31}P NMR spectroscopy of (a) 10 mmol JohnposAu(MeCN)SbF_6, (b) mixture of 10 mmol JohnposAu(MeCN)SbF_6 and 10 mmol **2a**, (c) mixture of 10 mmol

JohnposAu(MeCN)SbF_6 and 20 mmol **1a**, (d) mixture of 10 mmol JohnposAu(MeCN)SbF_6, 20 mmol 1a and 20 mmol **2a** in 0.5 mL $CDCl_3$.

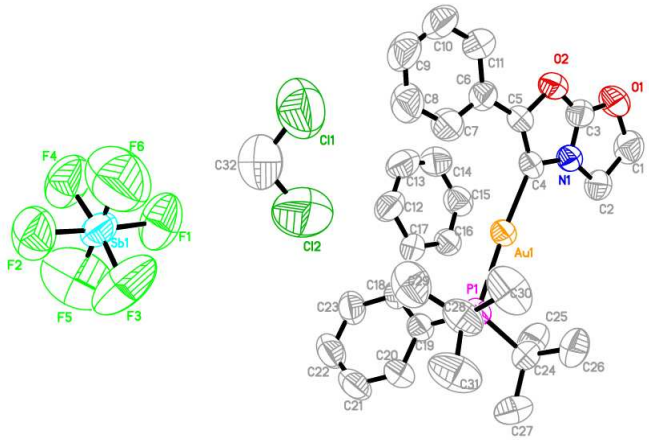


Figure 2. X-ray structure of JohnphosAu(**1a**)SbF_6. Hydrogen atoms have been omitted for clarity.

On the other hand, the reaction of **2a** with JohnphosAu(MeCN)SbF_6 gave JohnphosAu(**2a**)SbF_6. The structure of this complex was also confirmed by X-ray crystallography (Figure 3), and the corresponding ^{31}P NMR showing a chemical shift at 59.03 ppm (Figure 1b). Interestingly, upon addition of **2a** to the mixture of JohnphosAu(MeCN)SbF_6 and **1a**, the peak for JohnphosAu(**1a**)SbF_6 disappeared with concomitant formation of a new species showing a chemical shift at 64.63 ppm (Figure 1d). Although attempts to crystallize the corresponding three-component adduct was not successful, a new species was detected by high resolution mass spectrometry (HR-MS, m/z: 850.2901, Figure S2 In Supporting Information), which could be assigned to a complex of gold catalyst with **1a** and **2a**, namely JohnphosAu(**1a**)(**2a**)SbF_6.

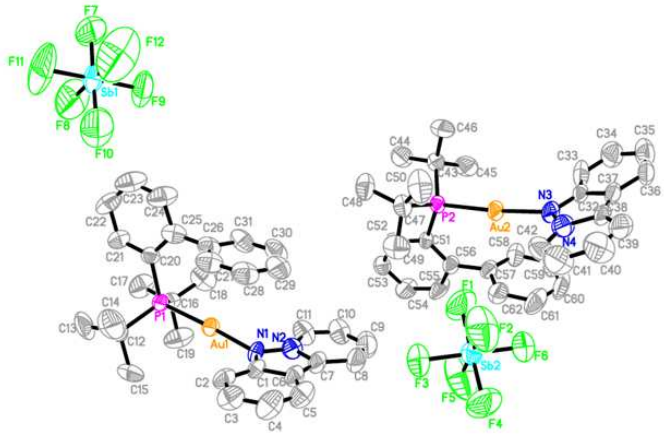


Figure 3. X-ray structure of JohnphosAu(**2a**)SbF_6. Hydrogen atoms have been omitted for clarity.

Kinetic studies for the gold-catalyzed reaction of **1a** and **2a** were further carried out to get better understanding of the reaction mechanism. The reaction was found to be first-order in JohnphosAu(MeCN)SbF_6 (Figure 4 and Figure S3 in Supporting Information) and zero-order in both **1a** and **2a** (Figure S4 and S5 in Supporting Information). Increasing the concentration of **2a** slightly depressed reaction rates, suggesting that **2a** may partially poison the gold catalyst. Varying temperature from 313 to 335 K (Figure 5 and Figure S6 in Supporting Information), activation parameters $\Delta H^{\ddagger}$ = 16.8 kcal mol^{-1} and $\Delta S^{\ddagger}$ = -19.1 cal mol^{-1} K^{-1} were obtained from Eyring plots. The negative $\Delta S^{\ddagger}$ value is consistent with our NMR experiments. Kinetics for the reactions of various *para*-substituted ynamides **1** with **2a** was also carried out. A fairly linear Hammett correlation between $\log(k_X/k_H)$ and σ was obtained with a reaction constant of ρ = -2.15 (Figure 6 and Figure S7 in Supporting Information), The large negative ρ value suggests that the transition state of the reaction is polarized with positive charge at the reaction center.

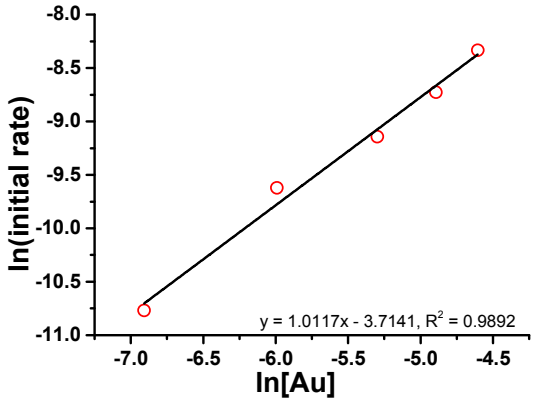


Figure 4. Plot of ln(initial rate) vs ln([Au]). y = 1.0117x – 3.7141, R^2 = 0.9892. The slope of the line is approximately 1, indicating that the rate for the reaction is first-order in JohnphosAu(MeCN)SbF_6.

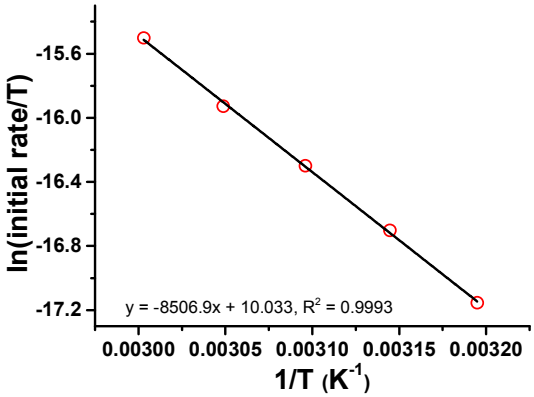


Figure 5. Plot of ln(initial rate/T) vs 1/T for the reaction between **1a** and **2a** in $CDCl_3$, [**1a**] = 0.10 M, [**2a**] = 60 mM, [Au] = 2.5 mM. Slope = -8.51×10^3, y-intercept = 1.00×10, R^2 = 0.999.

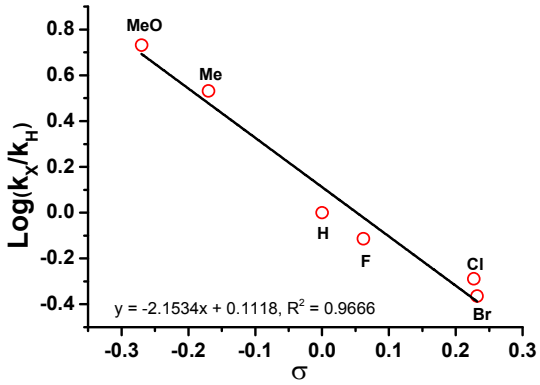
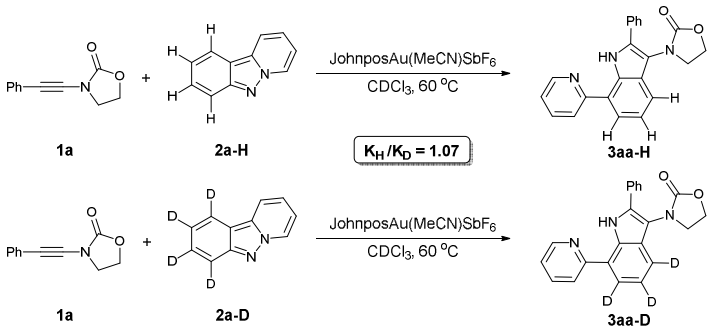


Figure 6. Hammett plot of $\log(k_X/k_H)$ vs σ for the reaction of **2a** with *para*-substituted ynamides **1** in $CDCl_3$ at 60 °C, [**1a**] = 0.10 M, [**2a**] = 60 mM, [Au] = 2.5 mM. Slope = -2.15, y-intercept = 0.11, $R^2 = 0.967$.



Scheme 3. Kinetic isotope effect experiments.

As C-H bond functionalization of the aromatic ring was involved in current transformation. To identify whether cleavage of the C-H bond at the ortho-position of pyrido[1,2-b]indazoles **2a** is involved as the rate-determined step, kinetic isotope effect of parallel experiments were carried out (Scheme 3 and Figure 7). As depicted, no significant kinetic isotope effect (k_H/k_D = 1.07) was observed, suggesting that C-H bond cleavage was not involved in the rate-determined step.

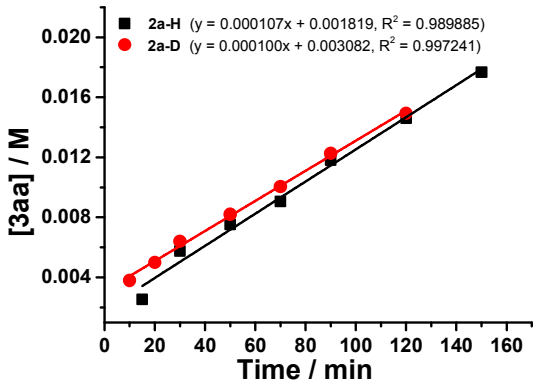
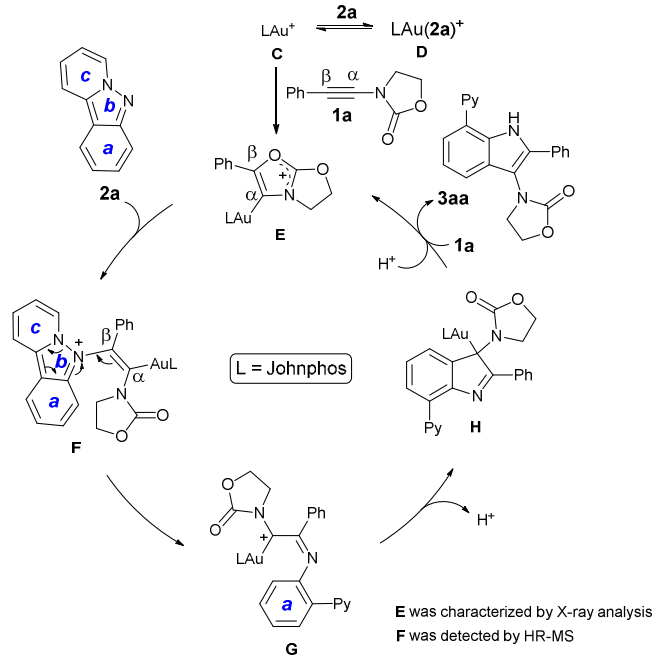


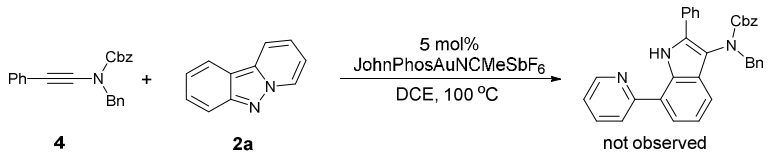
Figure 7. Kinetic profiles for the gold-catalyzed annulation of ynamides **1a** with pyrido[1,2-b]indazoles **2a-H** (black) and **2a-D** (red). Yields were obtained by ^{1}H MNR using dibromomethane as internal standard. Standard reaction conditions: [**1a**] = 0.10 M, [**2a**] = 0.12 M, [Au] = 5 mM in 2.0 mL $CDCl_3$ under argon at 60 ^{o}C.

Collectively, plausible mechanistic rationales for current indole synthesis were outlined in Scheme 4. Coordination of ynamide **1a** to the gold catalyst **C** would generate intermediate **E** bearing a transient five-membered ring. A nucleophilic attack of **E** by **2a** gave **F**. Ring opening of the pyrido[1,2-b]indazole (***b*** ring) led to the formation of intermediate **G**. Intramolecular sp^2 C-H bond functionalization taking place (**G→H**), followed by protodeauration and isomerization, would furnish the final product 3-aminoindole **3aa**. Since enhanced reaction rate and efficiency were observed by setting up electron-withdrawing groups onto a ring (Table 3 and Scheme S1 in Supporting Information),[25] pathways akin to Friedel-Craft-type alkylation or C-H bond insertion of gold carbene intermediate were unlikely.



Scheme 4. Mechanistic Rationale.

During the testing of the scope of ynamides, we found that the reaction of ynamides bearing sulfonyl protecting group on the nitrogen atom led to no formation of corresponding 3-amidoindoles (results not shown). Notably, when ynamide **4**, possessing a Cbz (benzyl carbomate) protected amide moiety, was employed instead of **1a**, the target indole was not obtained either (Scheme 5). These observations further highlight the critical role of oxazolidin-2-onyl moiety for current β-regioselective formal cycloaddition.



Scheme 5. The reaction of ynamide **4** with **2a**.

Conclusions

In summary, we have demonstrated a novel gold-catalyzed formal [3+2] cycloaddition of ynamides with pyrido[1,2-b]indazoles, furnishing 3-amido-7-(pyrid-2'-yl)indoles in good to excellent yields. Compared with previous relatively extensive studies on gold-catalyzed reactions of ynamides, current transformation has showcased an unusual β-site regioselective formal cycloadditon of pyrido[1,2-b]indazoles **2** to ynamides **1**, thus leading 3-amidoindoles exclusively. According to this activation mode, we believe that a number of new reactions which feature β-site regioselective addition of ynamides will be uncovered in the near future.

EXPERIMENTAL SECTION

General Information. JohnphosAu(MeCN)SbF_6,[16] ynamides **1**[26] and pyrido[1,2-b]indazoles **2**[17] were prepared according to literature methods. All reactions were carried out with standard Schlenk techniques under argon. All reagents were used as received from commercial suppliers unless otherwise stated. All solvents were purified by distillation following standard procedures. Reaction progress was monitored by thin layer chromatography (TLC) and components were visualized by observation under UV light at 254 nm. Flash column chromatography was performed using silica gel 60 (200-300 mesh). High resolution mass spectrometry was performed on UHR TOF LC/MS Mass Spectrometry. All ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra were recorded on a 400 MHz spectrometer (^{1}H 400 MHz, ^{13}C 100 MHz, ^{31}P 162 MHz) using $CDCl_3$ as solvent. Chemical shifts were reported in parts per million (ppm, δ). ^{1}H NMR spectra are referenced to the peak of tetramethylsilane (δ = 0.00) and reported as follows: chemical shift (ppm), multiplicity (s = singlet, t = triplet, q = quartet, m = multiplet) and coupling constant (Hz). ^{13}C NMR spectra are referenced to the solvent center peak of $CDCl_3$ (δ = 77.0). ^{31}P NMR spectra are referenced to the peak of H_3PO_4 (δ = 0.00).

Synthesis of pyrido[1,2-b]indazole 2

A solution of 2-phenylpyridine (2 mmol), $[Cp^*RhCl_2]_2$ (4 mol %), $PhI(OAc)_2$ (1.5 equiv) and *p*-$TsOH\cdot H_2O$ (1.5 equiv) in 15 mL acetone was stirred at room temperature for 15 min. After addition of NaN_3 (6 mmol), the reaction mixture was stirred at 50 °C for 16 h. Then the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using EA/PE as eluent to afford the azidation product 2-(2-azidophenyl)–pyridine **b** in 88% yield. 2-(2-Azidophenyl)pyridine **b** and dry dioxane (5 mL) were charged into a pressure tube under nitrogen. After stirred at 125 ^oC for 8 - 20 h, the solvent was removed on a rotary evaporator and the residue was purified by column chromatography on silica gel (ethyl acetate/petroleum ether = 10 : 1), affording the product pyrido[1,2-b]indazole **2a**.

^1H and ^{13}C NMR Spectra data for the prepared substrates

2-(2-azidophenyl)pyridine (**b**)

^1H NMR (400 MHz, $CDCl_3$) δ 8.71 (d, *J* = 4.4 Hz, 1H), 7.74-7.65 (m, 3H), 7.43 (t, *J* = 7.2 Hz, 1H), 7.26-7.22 (m, 3H); $^{13}C\{H\}$NMR (100 MHz, $CDCl_3$) δ155.7, 149.4, 137.1, 135.8, 132.1, 131.4, 129.8, 125.0, 124.8, 122.1, 118.7.

pyrido[1,2-b]indazole (2a)

^1H NMR (400 MHz, $CDCl_3$) δ 8.77 (d, *J* = 6.8 Hz, 1H), 8.08 (t, *J* = 6.8 Hz, 2H), 7.85 (d, *J* = 8.4 Hz, 1H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.15 (t, *J* = 6.8 Hz, 1H); $^{13}C\{H\}$NMR (100 MHz, $CDCl_3$) δ 149.6, 135.3, 128.4, 127.9, 121.9, 119.8, 119.7, 117.9, 116.2, 115.5, 115.1.

3-fluoropyrido[1,2-b]indazole (2b)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (d, *J* = 6.8 Hz, 1H), 8.02-8.96 (m, 2H), 7.41-7.27 (m, 2H), 7.16-7.12 (m, 1H), 7.00-6.94 (m, 1H); ^{13}C{H}NMR (100 MHz, $CDCl_3$) δ 163.3 (d, *J* = 244 Hz), 150.2 (d, *J* = 13 Hz), 135.5, 128.1, 122.9, 121.5 (d, *J* = 11 Hz), 117.5, 116.0, 112.1, 110.4 (d, *J* = 27 Hz), 99.4 (d, *J* = 24 Hz).

3-chloropyrido[1,2-b]indazole (2c)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (d, *J* = 6.8 Hz, 1H), 8.09 (d, *J* = 8.8 Hz, 1H), 8.00 (d, *J* = 8.8 Hz, 1H), 7.81 (s, 1H), 7.41 (t, *J* = 8.0 Hz, 1H), 7.23-7.16 (m, 2H); ^{13}C{H}NMR (100 MHz, $CDCl_3$) δ 150.0, 135.4, 134.3, 128.2, 122.8, 121.0, 120.9, 117.9, 116.6, 114.7, 113.6.

3-bromopyrido[1,2-b]indazole (2d)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (d, *J* = 6.8 Hz, 1H), 8.02 (d, *J* = 8.4 Hz, 1H), 7.96 (s, 1H), 7.87 (d, *J* = 8.4 Hz, 1H), 7.36 (t, *J* = 7.2 Hz, 1H), 7.27-7.17 (m, 2H); ^{13}C{H}NMR (100 MHz, $CDCl_3$) δ 150.3, 135.3, 128.1, 123.1, 122.8, 122.4, 121.1, 117.9, 117.8, 116.6, 113.8.

3-methylpyrido[1,2-b]indazole (2e)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (d, *J* = 5.6 Hz, 1H), 8.07 (d, *J* = 8.2 Hz, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.60 (s, 1H), 7.33 (t, *J* = 7.2 Hz, 1H), 7.16-7.06 (m, 2H), 2.57 (s, 3H); ^{13}C{H}NMR (100 MHz, $CDCl_3$) δ 150.3, 138.6, 135.3, 127.9, 122.4, 121.9, 119.3, 117.6, 115.7, 114.3, 113.3, 22.4.

3-methoxypyrido[1,2-b]indazole (2f)

Pale yellow solid; Yield: 244 mg, 61 %; mp: 102-104 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (d, *J* = 6.8 Hz, 1H), 8.00 (d, *J* = 8.8 Hz, 1H), 7.93 (d, *J* = 8.8 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.12 – 7.07 (m, 2H), 6.90 (d, *J* = 8.8 Hz, 1H), 3.94 (s, 4H); ^{13}C{H}NMR (100 MHz, $CDCl_3$) δ 160.7, 151.2, 135.4, 127.9, 122.3, 120.6, 117.1, 114.9, 113.5, 110.0, 93.8, 55.3; IR (KBr): $\tilde{\nu}$ = 1649.0, 1604.5, 1557.7, 1475.2,

1431.5, 1324.5, 1290.3, 1214.9, 1197.9, 1163.3, 801.9, 758.7, 740.6 cm^{-1}; HRMS (EI) m/z: $[M + H]^+$ calcd for $C_{12}H_{11}N_2O$, 199.0871; found: 199.0866.

methylpyrido[1,2-b]indazole-3-carboxylate (2g)

Pale yellow solid; Yield: 80.0 mg, 15 %; mp: 180-182 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 8.83 (d, *J* = 6.4 Hz, 1H), 8.61 (s, 1H), 8.15 (dd, *J* = 16.0, 8.4 Hz, 2H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.42 (t, *J* = 7.2 Hz, 1H), 7.27 (s, 1H), 4.00 (s, 3H); $^{13}C\{H\}$NMR (100 MHz, $CDCl_3$) δ 167.5, 149.0, 135.3, 130.1, 128.2, 122.5, 119.9, 119.7, 118.9, 118.6, 117.6, 117.2, 52.3; IR (KBr): ṽ = 1715.2, 1432.8, 1366.5, 1303.1, 1219.8, 1144.2, 1081.6, 751.7, 720.6 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{13}H_{11}N_2O_2$, 227.0821; found: 227.0815.

3-phenylpyrido[1,2-b]indazole (2h)

Pale yellow solid; Yield: 297 mg, 61 %; mp: 120-121 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 8.80 (d, *J* = 6.4 Hz, 1H), 8.15 (d, *J* = 7.2 Hz, 2H), 8.03 (s, 1H), 7.75 (d, *J* = 7.2 Hz, 2H), 7.52-7.36 (m, 5H), 7.21-7.18 (t, *J* = 6.0 Hz, 1H); $^{13}C\{H\}$NMR (100 MHz, CDCl3) δ 150.3, 141.7, 141.6, 135.3, 128.8, 128.0, 127.6, 127.4, 122.1, 120.14, 120.07, 117.9, 116.2, 114.4, 113.4; IR (KBr): ṽ = 1644.7, 1596.9, 1533.4, 1507.6, 1421.1, 1362.7, 1339.1, 1212.6, 753.8, 741.3, 722.0 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{17}H_{13}N_2$, 245.1079; found: 245.1073.

2-chloropyrido[1,2-b]indazole (2i)

^1H NMR (400 MHz, $CDCl_3$) δ 8.72 (d, *J* = 6.8 Hz, 1H), 8.00-7.98 (m,2H), 7.74 (d, *J* = 9.2 Hz, 1H), 7.46 (dd, *J* = 9.2, 2.0 Hz, 1H), 7.34-7.30 (m, 1H), 7.18-7.15 (m, 1H); $^{13}C\{H\}$NMR (100 MHz, $CDCl_3$) δ 147.9, 134.7, 129.3, 128.0, 125.0, 122.3, 118.8, 118.0, 117.0, 116.6, 115.6.

2-bromopyrido[1,2-b]indazole (2j)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (d, *J* = 6.4 Hz, 1H), 8.23 (s, 1H), 8.08 (d, *J* = 8.4 Hz, 1H), 7.67 (dd, *J* = 46, 8.8 Hz, 2H), 7.40 (t, *J* = 7.2 Hz, 1H), 7.23 (t, *J* = 6.4 Hz, 1H); ^{13}C{H}NMR (100 MHz, $CDCl_3$) δ 148.1, 134.6, 131.7, 128.1, 122.5, 122.2, 118.0, 117.3, 116.8, 116.4, 112.5.

1-methylpyrido[1,2-b]indazole (2k)

Pale yellow oil; Yield: 96.0 mg, 26 %; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (d, *J* = 6.4 Hz, 1H), 8.13 (d, *J* = 8.8 Hz, 1H), 7.69 (d, *J* = 8.8 Hz, 1H), 7.47-7.25 (m, 2H), 7.14 – 6.96 (m, 2H), 2.80 (s, 3H); ^{13}C{H}NMR (100 MHz, $CDCl_3$) δ 149.7, 135.6, 132.1, 128.3, 127.8, 121.8, 120.2, 119.5, 115.6, 114.8, 113.0, 20.3; IR (KBr): ṽ = 1635.6, 1599.4, 1532.4, 1511.9, 1440.0, 1218.4, 1142.8, 785.7, 740.5, 718.4 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{12}H_{11}N_2$, 183.0922; found: 183.0917.

1-chloropyrido[1,2-b]indazole (2l)

Pale yellow solid; Yield:132 mg, 32 %; mp: 90-91 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (d, *J* = 6.8 Hz, 1H), 8.53 (d, *J* = 8.8 Hz, 1H), 7.72 (d, *J* = 8.4 Hz, 1H), 7.46-7.36 (m, 2H), 7.22-7.17 (m, 2H); ^{13}C{H}NMR (100 MHz, $CDCl_3$) δ 150.5, 135.1, 128.6, 127.9, 127.0, 122.7, 120.1, 119.7, 116.8, 114.1, 113.3; IR (KBr): ṽ = 1642.0, 1600.3, 1511.5, 1436.4, 1408.6, 1358.9, 1215.7, 1137.4, 950.9, 784.2, 740.7, 712.9 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{11}H_8ClN_2$, 203.0376; found: 203.0371.

8-methylpyrido[1,2-b]indazole (2m)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (s, 1H), 8.03 (dd, *J* = 16, 8.4 Hz, 2H), 7.82 (d, *J* = 8.8 Hz, 1H), 7.54 (t, *J* = 7.6 Hz, 1H), 7.22-7.19 (m, 2H), 2.49 (s, 3H); ^{13}C{H}NMR (100 MHz, $CDCl_3$) δ 149.5, 133.7, 127.9, 126.5, 126.2, 124.7, 119.5, 119.4, 117.1, 115.4, 115.1, 18.58.

8-chloropyrido[1,2-b]indazole (2n)

Pale yellow solid; Yield: 110 mg, 27 %; mp: 157-159 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (d, *J* = 0.8 Hz, 1H), 7.99 (dd, *J* = 12.4, 8.4 Hz, 2H), 7.83 (d, *J* = 8.8 Hz, 1H), 7.58-7.54 (m, 1H), 7.28-7.22 (m,

2H); $^{13}C\{H\}$NMR (100 MHz, $CDCl_3$) δ 150.0, 133.7, 128.6, 126.1, 124.2, 123.0, 120.6, 119.5, 117.9, 115.9, 115.2; IR (KBr): $\tilde{\nu}$ = 1598.8, 1511.6, 1436.8, 1354.1, 1329.0, 1315.2, 1074.6, 798.7, 740.6, 710.4 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{11}H_8ClN_2$, 203.0376; found: 203.0371.

9-methylpyrido[1,2-b]indazole (2o)

^1H NMR (400 MHz, $CDCl_3$) δ 8.64 (d, *J* = 7.2 Hz, 1H), 8.02 (d, *J* = 8.0 Hz, 1H), 7.84-7.78 (m, 2H), 7.53 (t, *J* = 7.6 Hz, 1H), 7.17 (t, *J* = 7.6 Hz, 1H), 6.98-6.97(m, 1H), 2.51 (s, 3H); $^{13}C\{H\}$NMR (100 MHz, $CDCl_3$) δ 150.0, 135.4, 133.0, 128.3, 127.2, 119.8, 119.1, 118.5, 116.8, 115.3, 114.5, 21.2.

pyrimido[1,2-b]indazole (2p)

^1H NMR (400 MHz, $CDCl_3$) δ 8.98 (dd, *J* = 6.8, 1.2 Hz, 1H), 8.63 (d, *J* = 2.4 Hz, 1H), 8.33 (d, *J* = 8.0 Hz, 1H), 7.85 (d, *J* = 8.4 Hz, 1H), 7.66 (t, *J* = 7.2 Hz, 1H), 7.34 (t, *J* = 7.2 Hz, 1H), 7.21 (dd, *J* = 6.8, 4.0 Hz, 1H); $^{13}C\{H\}$NMR (100 MHz, $CDCl_3$) δ 151.3, 145.2, 143.8, 133.7, 130.0, 121.1, 120.7, 116.1, 113.3, 111.6.

Au-catalyzed cycloaddition of ynamides 1 with pyrido[1,2-b]indazoles 2

General method: A pressure tube equipped with a magnetic stirrer bar was charged with JohnphosAu(MeCN)SbF_6 (5 mol %), ynamide **1** (0.2 mmol), pyrido[1,2-b]indazole **2** (0.24 mmol) and solvent (1 mL). The reaction was stirred for 11 h at 100 ^oC. Then the solvent was removed under vacuum, and the residue was purified by column chromatography on silica gel (ethyl acetate/petroleum ether = 2 : 1), providing the desired compound **3**.

Method for 3fa, **3ga**, **3ha**, **3ma**:

To a solution of JohnphosAu(MeCN)SbF_6 (5 mol %) in dry DCE was added ynamide **1** (0.2 mmol) and pyrido[1,2-b]indazole **2** (0.24 mmol). The reaction mixture was stirred 4 h at 100 ^oC,

then another portion of JohnphosAu(MeCN)SbF_6 (5 mol%) was added. After the reaction was complete (detected by TLC), the solvent was removed under vacuum, and the residue was purified by column chromatography using PE/EA as eluent to provide the desired compound.

^{1}H and ^{13}C NMR Spectra data for the prepared products

3-(2-phenyl-7-(pyridin-2-yl)-1H-indol-3-yl)oxazolidin-2-one (3aa)

Pale yellow solid; Yield: 67.4 mg, 95 %; mp 142-143 ^{o}C; R_f = 0.30 (PE/EA = 2:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.67 (s, 1H), 8.73-8.71 (m, 1H), 8.03 (d, *J* = 8.0 Hz, 1H), 7.83-7.75 (m, 4H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 2H), 7.44-7.41 (m, 1H), 7.28-7.22 (m, 2H), 4.53 (d, *J* = 8.0 Hz,2H), 3.85 (d, *J* = 8.0 Hz,2H); ^{13}C{H}NMR (100 MHz, $CDCl_3$) δ 158.1, 157.4, 148.6, 136.7, 134.2, 133.16, 131.2, 129.2, 128.5, 127.2, 126.3, 121.6, 121.0, 120.4, 120.3, 119.9, 119.5, 110.1, 62.6, 47.6; IR (KBr): $\tilde{\nu}$ = 3686, 3308, 1750, 1590, 1438, 1271, 1110, 778, 689 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{22}H_{18}N_3O_2$, 356.1399; found: 356.1394.

3-(2-(4-methoxyphenyl)-7-(pyridin-2-yl)-1H-indol-3-yl)oxazolidin-2-one (3ba)

Pale yellow solid; Yield: 70.5 mg, 91 %; mp: 170-171 ^{o}C; R_f = 0.15 (PE/EA = 2:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.57 (s, 1H), 8.69 (d, *J* = 4.0 Hz, 1H), 7.99 (d, *J* = 8.4 Hz, 1H), 7.78-7.75 (m, 2H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.59 (d, *J* = 7.6 Hz, 1H), 7.25-7.19 (m, 2H), 7.04 (d, *J* = 8.4 Hz, 2H), 4.50 (t, *J* = 8.0 Hz, 2H), 3.86 (s, 3H), 3.82 (t, *J* = 8.0 Hz, 2H);^{13}C{H}NMR (100 MHz, $CDCl_3$) δ 159.8, 158.1, 157.4, 148.5, 136.7, 134.2, 132.9, 128.5, 126.4, 123.6, 121.5, 120.7, 120.3, 120.0, 119.8, 119.1, 114.5, 109.2, 62.5, 55.3, 47.4; IR (KBr): $\tilde{\nu}$ = 3295, 1746, 1590, 1513,

1262, 1032, 775 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{23}H_{20}N_3O_3$, 386.1505; found: 386.1499.

3-(7-(pyridin-2-yl)-2-(p-tolyl)-1H-indol-3-yl)oxazolidin-2-one (3ca)

White solid; Yield: 68.1 mg, 92 %; mp: 237-238 ^oC; R_f = 0.33 (PE/EA = 2:1); ^1H NMR (400 MHz, $CDCl_3$) 11.63 (s, 1H), 8.71 (d, *J* = 3.6 Hz, 1H), 8.02 (d, *J* = 8.0 Hz, 1H), 7.82-7.78 (m, 2H), 7.66-7.61 (m, 3H), 7.34-7.21 (m, 4H), 4.53 (t, *J* = 8.0 Hz, 2H), 3.84 (t, *J* = 8.0 Hz, 2H), 2.44 (s, 3H);$^{13}C\{H\}$NMR (100 MHz, $CDCl_3$) δ 158.1, 157.4, 148.6, 138.5, 136.7, 134.4, 133.0, 129.8, 128.3, 127.1, 126.4, 121.5, 120.9, 120.4, 120.1, 119.9, 119.3, 109.7, 62.6, 47.5, 21.4; IR (KBr): $\tilde{\nu}$ = 3327, 1745, 1413, 1268, 1032, 817, 777, 656 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{23}H_{20}N_3O_2$, 370.1556; found: 370.1550.

3-(2-(4-ethylphenyl)-7-(pyridin-2-yl)-1H-indol-3-yl)oxazolidin-2-one (3da)

Pale yellow solid; Yield, 76.4 mg, 99 %; mp: 127-128 ^oC; R_f = 0.25 (PE/EA = 2:1); ^1H NMR (400 MHz, $CDCl_3$) δ 11.63 (s, 1H), 8.68 (d, *J* = 4.0 Hz, 1H), 7.99 (d, *J* = 7.6 Hz, 1H), 7.78-7.59(m, 5H), 7.36-7.19 (m, 4H), 4.51 (t, *J* = 8.0 Hz, 2H), 3.83 (t, *J* = 8.0 Hz, 2H), 2.72 (q, *J* = 7.6 Hz, 2H), 1.30 (t, *J* = 7.6 Hz, 3H); $^{13}C\{H\}$NMR (100 MHz, $CDCl_3$) δ 158.1, 157.4, 148.5, 144.7, 136.7, 134.3, 133.0, 128.6, 128.5, 127.1, 126.4, 121.5, 120.8, 120.3, 120.1, 119.8, 119.3, 109.7, 62.5, 47.5, 28.7, 15.4; IR (KBr): $\tilde{\nu}$ = 3327, 2965, 1742, 1588, 1415, 1268, 1102, 773, 638 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{24}H_{22}N_3O_2$, 384.1712; found: 384.1707.

3-(2-(4-fluorophenyl)-7-(pyridin-2-yl)-1H-indol-3-yl)oxazolidin-2-one(3ea)

Pale yellow solid, Yield, 74.2 mg, 99 %; mp: 183-184 ^oC; R_f = 0.33 (PE/EA = 2:1); ^1H NMR (400 MHz, $CDCl_3$) δ 11.63 (s, 1H), 8.69 (d, *J* = 3.6 Hz, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.79-7.70

(m, 4H), 7.59 (d, *J* = 7.6 Hz, 1H), 7.26-7.18 (m, 4H), 4.51 (t, *J* = 8.0 Hz, 2H), 3.82 (t, *J* = 8.0 Hz, 2H); $^{13}C\{H\}$NMR (100 MHz, $CDCl_3$) δ 162.7 (d, *J* =248 Hz), 158.1, 157.2, 148.5, 136.7, 133.4, 133.0, 129.0 (d, *J* = 8.0 Hz), 127.3 (d, *J* = 3.0 Hz), 126.2, 121.6, 120.9, 120.5, 120.3, 119.8, 119.3, 116.2 (d, *J* = 21.0 Hz), 110.0, 62.5, 47.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.4; IR (KBr): $\tilde{\nu}$ = 3308, 1746, 1507, 1412, 1230, 1113, 1032, 775, 661 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{22}H_{17}FN_3O_2$, 374.1305; found: 374.1299.

3-(2-(4-chlorophenyl)-7-(pyridin-2-yl)-1H-indol-3-yl)oxazolidin-2-one (3fa)

White solid; Yield: 67.7 mg, 87 %; mp: 215-216 °C; R_f = 0.33 (PE/EA = 2:1); ^1H NMR (400 MHz, $CDCl_3$) δ 11.68 (s, 1H), 8.71 (d, *J* = 4.0 Hz, 1H), 8.02 (d, *J* = 8.4 Hz, 1H), 7.81-7.79 (m, 2H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.61 (d, *J* = 7.6 Hz, 1H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.28-7.22 (m, 2H), 4.53 (t, *J* = 8.0 Hz, 2H), 3.84 (t, *J* = 8.0 Hz, 2H); $^{13}C\{H\}$NMR (100 MHz, $CDCl_3$) δ 158.1, 157.3, 148.6, 136.8, 134.4, 133.2, 133.1, 129.6, 129.4, 128.4, 126.2, 121.7, 121.0, 120.6, 120.5, 119.9, 119.4, 110.5, 62.6, 47.6; IR (KBr): $\tilde{\nu}$ = 3369, 1758, 1742, 1493, 1408, 1271, 1252, 1118, 773, 592 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{22}H_{17}ClN_3O_2$, 390.1009; found: 390.1004.

3-(2-(4-bromophenyl)-7-(pyridin-2-yl)-1H-indol-3-yl)oxazolidin-2-one (3ga)

Pale yellow solid; Yield: 63.6 mg, 73 %; mp: 198-199 °C; R_f = 0.33 (PE/EA = 2:1); ^1H NMR (400 MHz, $CDCl_3$) δ 11.68 (s, 1H), 8.71 (d, *J* = 3.6 Hz, 1H), 8.02 (d, *J* = 8.0 Hz, 1H), 7.82-7.79 (m, 2H), 7.65-7.60 (m, 5H), 7.28-7.22 (m, 2H), 4.53 (t, *J* = 8.0 Hz, 2H), 3.84 (t, *J* = 8.0 Hz, 2H); $^{13}C\{H\}$NMR (100 MHz, $CDCl_3$) δ 158.1, 157.3, 148.6, 136.8, 133.3, 133.1, 132.3, 130.0, 128.7, 126.2, 122.6, 121.7, 121.0, 120.62, 120.57,, 119.9, 119.5, 110.5, 62.6, 47.6; IR (KBr): $\tilde{\nu}$ = 3373, 1739, 1592, 1414, 1271, 1034, 769, 745, 582 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{22}H_{17}BrN_3O_2$, 434.0504; found: 434.0499.

3-(2-(3-chlorophenyl)-7-(pyridin-2-yl)-1H-indol-3-yl)oxazolidin-2-one(3ha)

White solid; Yield, 72.6 mg, 93 %; mp: 192-193 ^{o}C; R_f = 0.33 (PE/EA = 2:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.71 (s, 1H), 8.76-8.74 (m, 1H), 8.04 (d, *J* = 8.4 Hz, 1H), 7.85-7.80 (m, 2H), 7.73 (t, *J* = 2.0 Hz, 1H), 7.67-7.62 (m, 2H), 7.47-7.38 (m, 2H), 7.30-7.24 (m, 2H), 4.58-4.54 (m, 2H), 3.89-3.85 (m, 2H); ^{13}C{H}NMR (100 MHz, $CDCl_3$) δ 158.0, 157.2, 148.6, 136.8, 135.1, 133.3, 132.9, 132.6, 130.5, 128.4, 127.0, 126.1, 125.4, 121.7, 121.1, 120.70, 120.65, 119.9, 119.6, 110.9, 62.6, 47.6;IR (KBr): $\tilde{\nu}$ = 3676, 3336, 3055, 2909, 1739, 1594, 1424, 1272, 1119, 769, 676 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{22}H_{17}ClN_3O_2$, 390.1009; found: 390.1004.

3-(2-(2-chlorophenyl)-7-(pyridin-2-yl)-1H-indol-3-yl)oxazolidin-2-one (3ia)

Pale yellow solid; Yield: 68.5 mg, 88 %; mp: 144-145 ^{o}C; R_f = 0.33 (PE/EA = 2:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.78 (s, 1H), 8.67 (d, *J* = 3.2 Hz, 1H), 8.03 (d, *J* = 8.0 Hz, 1H), 7.84-7.66 (m, 4H), 7.57-7.54 (m, 1H), 7.41-7.39 (m, 2H), 7.30-7.20 (m, 2H), 4.44 (t, *J* = 8.0 Hz, 2H), 3.80 (t, *J* = 8.0 Hz, 2H); ^{13}C{H}NMR (100 MHz, $CDCl_3$) δ 157.7, 157.2, 148.5, 136.6, 133.1, 132.9, 132.1, 131.1, 130.2, 130.1, 130.0, 127.2, 125.2, 121.5, 121.0, 120.4, 120.3, 119.79, 119.76, 111.9, 62.5, 47.5; IR (KBr): $\tilde{\nu}$ = 3357, 1744, 1430, 1399, 1221, 1034, 767, 744 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{22}H_{17}ClN_3O_2$, 390.1009; found: 390.1004.

3-(2-(naphthalen-1-yl)-7-(pyridin-2-yl)-1H-indol-3-yl)oxazolidin-2-one (3ja)

White solid, Yield: 80.9 mg, 99 %; mp: 123-124 ^{o}C; R_f = 0.33 (PE/EA = 2:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.63 (s, 1H), 8.57 (d, *J* = 4.4 Hz, 1H), 8.05 (d, *J* = 8.0 Hz, 2H), 8.00-7.95 (m, 2H), 7.86 (d, *J* = 7.2 Hz, 1H), 7.81-7.73 (m, 3H), 7.63-7.49 (m, 3H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.19-7.16 (m, 1H), 4.21 (t, *J* = 8.0 Hz, 2H), 3.53 (d, *J* = 8.0 Hz, 2H); ^{13}C{H}NMR (100 MHz, $CDCl_3$) δ 157.6, 157.4, 148.5, 136.7, 133.6, 133.2, 132.7, 131.8, 129.4, 128.8, 128.5, 128.4, 127.1, 126.4, 125.6, 125.5, 121.5, 121.0, 120.4,

120.3, 119.9, 119.8, 112.3, 62.3, 47.4; IR (KBr): $\tilde{\nu}$ = 3337, 1749, 1589, 1397, 1270, 1103, 772, 656 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{26}H_{20}N_3O_2$, 406.1556; found: 406.1550.

3-(2-(naphthalen-2-yl)-7-(pyridin-2-yl)-1H-indol-3-yl)oxazolidin-2-one (3ka)

Pale yellow solid; Yield, 66.1 mg, 82 %; mp: 115-116 ^oC; R_f = 0.30 (PE/EA = 2:1); ^1H NMR (400 MHz, $CDCl_3$) δ 11.76 (s, 1H), 8.71 (d, *J* = 4.0 Hz, 1H), 8.18 (s, 1H), 8.00-7.75 (m, 7H), 7.64 (d, *J* = 7.6 Hz, 1H), 7.56-7.50 (m, 2H), 7.28-7.19 (m, 2H), 4.49 (t, *J* = 8.0 Hz, 2H), 3.80 (t, *J* = 8.0 Hz, 2H); $^{13}C\{H\}$NMR (100 MHz, $CDCl_3$) δ 158.1, 157.3, 148.6, 136.7, 134.1, 133.4, 133.3, 133.0, 128.9, 128.5, 128.3, 127.7, 126.7, 126.6, 126.33, 126.26, 124.7, 121.6, 120.9, 120.5, 120.4, 119.9, 119.5, 110.5, 62.6, 47.5; IR (KBr): $\tilde{\nu}$ = 3336, 1749, 1590, 1398, 1270, 1110, 771, 747,643 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{26}H_{20}N_3O_2$, 406.1556; found: 406.1550.

3-(2-butyl-7-(pyridin-2-yl)-1H-indol-3-yl)oxazolidin-2-one (3la)

Pale yellow solid; Yield: 27.9 mg, 42 %; mp: 142-143 ^oC; R_f = 0.30 (PE/EA = 2:1); ^1H NMR (400 MHz, $CDCl_3$) δ 11.21 (s, 1H), 8.72 (d, *J* = 3.6 Hz, 1H), 8.00 (d, *J* = 8.0 Hz, 1H), 7.81-7.77 (m, 1H), 7.72 (d, *J* = 7.2 Hz, 1H), 7.50 (d, *J* = 7.6 Hz, 1H), 7.24-7.19 (m, 2H), 4.58 (t, *J* = 8.0 Hz, 2H), 4.01 (t, *J* = 8.0 Hz, 2H), 2.83 (t, *J* = 8.0 Hz, 2H), 1.80-1.72 (m, 2H), 1.52-1.42 (m, 2H), 0.98 (t, *J* = 7.6 Hz, 3H); $^{13}C\{H\}$NMR (100 MHz, $CDCl_3$) δ 157.7, 157.6, 148.5, 137.0, 136.6, 132.5, 125.7, 121.4, 120.4, 120.0, 119.9, 119.7, 119.1, 118.4, 109.6, 62.3, 48.3, 31.0, 25.6, 22.6, 13.8; IR (KBr): $\tilde{\nu}$ = 3364, 2921, 1750, 1467, 1404, 1263, 771 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{20}H_{22}N_3O_2$, 336.1712; found: 336.1707.

(S)-4-benzyl-3-(2-phenyl-7-(pyridin-2-yl)-1H-indol-3-yl)oxazolidin-2-one (3ma)

White solid; Yield: 67.7 mg, 76 %; mp: 86-87 ^{o}C; R_f = 0.50 (PE/EA = 2:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.69 (s, 1H), 8.73 (d, *J* = 4.4 Hz, 1H), 8.04 (d, *J* = 8.0 Hz, 1H), 7.80 (dd, *J* = 15.6, 7.6 Hz, 3H), 7.66 (d, *J* = 7.6 Hz, 1H), 7.55-7.42 (m, 3H), 7.31-7.22 (m, 2H), 7.15-7.13 (m, 3H), 6.85 (d, *J* = 6.0 Hz, 2H), 4.37-4.21 (m, 3H), 2.86 (d, *J* = 12.8 Hz, 1H), 2.50 (s, 1H); ^{13}C{H}NMR (100 MHz, $CDCl_3$) δ 157.4, 148.6, 136.8, 135.6, 133.3, 131.3, 129.1, 128.8, 128.6, 128.6, 127.6, 126.8, 121.6, 121.0, 120.6, 120.4, 120.0, 119.6, 108.7, 67.9, 59.7, 39.2; IR (KBr): $\tilde{\nu}$ = 3339, 2924, 1757, 1590, 1439, 1396, 1270, 1119, 769, 698 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{29}H_{24}N_3O_2$, 446.1869; found: 446.1863.

3-(4-fluoro-2-phenyl-7-(pyridin-2-yl)-1H-indol-3-yl)oxazolidin-2-one(3ab)

Pale yellow solid, Yield: 74.0 mg, 99 %; mp: 186-187 ^{o}C; R_f = 0.30 (PE/EA = 2:1); ^{1}H NMR (400 MHz, CD_3CN) δ 12.02 (s, 1H), 8.78 (d, *J* = 4.0 Hz, 1H),8.08 (d, *J* = 8.4 Hz, 1H), 7.92-7.82 (m, 4H), 7.59-7.55 (m, 2H), 7.50-7.46 (m, 1H), 7.35-7.32 (m, 1H), 6.99-6.94 (m, 1H), 4.56-4.49 (m, 2H), 4.04-3.98 (m, 1H), 3.86-3.81 (m, 1H); ^{13}C{H}NMR (100 MHz, $CDCl_3$) δ 158.6, 156.6, 156.4 (d, *J* = 248 Hz), 148.4, 136.8, 135.8 (d, *J* = 11.0 Hz), 135.1, 130.5, 129.1, 128.7, 127.2, 121.4, 121.1 (d, *J* = 8.0 Hz), 119.6, 117.5 (d, *J* = 4.0 Hz), 114.9 (d, *J* = 20.0 Hz), 108.3, 105.9 (d, *J* = 20.0 Hz), 62.6, 48.6 (d, *J* = 3.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -120.2; IR (KBr): $\tilde{\nu}$ = 3321, 1754, 1593, 1468, 1270, 1124, 760, 694 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{22}H_{17}FN_3O_2$, 374.1305; found: 374.1299.

3-(4-chloro-2-phenyl-7-(pyridin-2-yl)-1H-indol-3-yl)oxazolidin-2-one (3ac)

Pale yellow solid, Yield: 76.2 mg, 97 %; mp: 231-232 ^{o}C; R_f = 0.33 (PE/EA = 2:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.95 (s, 1H), 8.66 (d, *J* = 3.6 Hz, 1H), 7.94 (d,*J* = 8.4 Hz, 1H), 7.77-7.64 (m, 4H), 7.54-7.43 (m, 3H), 7.23-7.17 (m, 2H), 4.62-4.56 (m, 1H), 4.49-4.42 (m, 1H), 4.09-4.02

(m, 1H), 3.75-3.70 (m, 1H); $^{13}C\{H\}$NMR (100 MHz, $CDCl_3$) δ 159.0, 156.6, 148.5, 136.9, 136.6, 134.5, 130.5, 129.2, 128.9, 127.4, 125.8, 123.4, 121.8, 121.4, 120.7, 120.0, 119.5, 109.4, 62.5, 49.1; IR (KBr): $\tilde{\nu}$ = 3311, 1751, 1603, 1407, 1244, 1122, 760, 694cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{22}H_{17}ClN_3O_2$, 390.1009; found: 390.1004.

3-(4-bromo-2-phenyl-7-(pyridin-2-yl)-1H-indol-3-yl)oxazolidin-2-one (3ad)

White solid; Yield: 82.0 mg, 94 %; mp: 254-255 ^oC; R_f = 0.33 (PE/EA = 2:1); ^1H NMR (400 MHz, $CDCl_3$) δ 11.98 (s, 1H), 8.66 (d, *J* = 4.0 Hz, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.79-7.75 (m, 3H), 7.59-7.43 (m, 4H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.23-7.20 (m, 1H), 4.63-4.57 (m, 1H), 4.48-4.42 (m, 1H), 4.10-4.04 (m, 1H), 3.73-3.67 (m, 1H); $^{13}C\{H\}$NMR (100 MHz, $CDCl_3$) δ 159.0, 156.5, 148.5, 136.9, 136.8, 134.3, 130.4, 129.2, 128.9, 127.4, 124.8, 124.6, 121.8, 121.0, 120.0, 119.9, 113.6, 109.7, 62.4, 49.0; IR (KBr): $\tilde{\nu}$ = 3272, 1751, 1602, 1409, 1120, 776, 692 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{22}H_{17}BrN_3O_2$, 434.0504; found: 434.0499.

3-(4-methyl-2-phenyl-7-(pyridin-2-yl)-1H-indol-3-yl)oxazolidin-2-one (3ae)

Pale yellow solid; Yield: 64.0 mg, 87 %; mp: 168-169 ^oC; R_f = 0.33 (PE/EA = 2:1); ^1H NMR (400 MHz, $CDCl_3$) δ 11.89 (s, 1H), 8.66 (d, *J* = 4.0 Hz, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.78-7.66 (m, 4H), 7.54-7.41 (m, 3H), 7.20-7.17 (m, 1H), 6.98 (d, *J* = 7.6 Hz, 1H), 4.55-4.38 (m, 2H), 3.87-3.65 (m, 2H), 2.68 (s, 3H); $^{13}C\{H\}$NMR (100 MHz, $CDCl_3$) δ 158.8, 157.5, 148.4, 136.6, 134.7, 133.4, 131.3, 131.1, 129.2, 128.4, 127.3, 125.5, 122.2, 121.2, 120.4, 119.6, 118.7, 110.1, 62.3, 48.8, 18.6; IR (KBr): $\tilde{\nu}$ = 3264, 1744, 1604, 1405, 1220, 1125, 1030, 764, 693 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{23}H_{20}N_3O_2$, 370.1556; found: 370.1550.

3-(4-methoxy-2-phenyl-7-(pyridin-2-yl)-1H-indol-3-yl)oxazolidin-2-one (3af)

White solid; Yield: 58.8 mg, 76 %; mp: 185-186 ^{o}C; R_f = 0.15 (PE/EA = 2:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.77 (s, 1H), 8.65 (d, *J* = 4.0 Hz, 1H), 7.92-7.70 (m, 4H), 7.52-7.38 (m, 3H), 7.17-7.14(m, 1H), 6.63 (d, *J* = 8.4 Hz, 1H), 4.57-4.42 (m, 2H), 4.10-4.03 (m, 1H), 4.00 (s, 3H), 3.76-3.71 (m, 1H); ^{13}C{H}NMR (100 MHz, $CDCl_3$) δ 159.4, 157.4, 154.6, 148.4, 136.5, 134.9, 133.6, 131.1, 129.0, 128.1, 127.1, 121.7, 120.6, 119.1, 116.0, 114.7, 110.2, 100.8, 62.7, 55.8, 49.3; IR (KBr): $\tilde{\nu}$ = 3323, 1738, 1600, 1466, 1259, 1108, 788, 764, 656 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{23}H_{20}N_3O_3$, 386.1505; found: 386.1499.

Methyl3-(2-oxooxazolidin-3-yl)-2-phenyl-7-(pyridin-2-yl)-1H-indole-4-carboxylate (**3ag**)

Yellow solid; Yield: 83.6 mg, 99 %; mp: 170-171 ^{o}C; R_f = 0.10 (PE/EA = 2:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.18 (s, 1H), 8.69 (d, *J* = 4.8 Hz, 1H), 8.03 (d, *J* = 8.4 Hz, 1H), 7.86-7.73 (m, 5H), 7.55-7.43 (m, 3H), 7.27-7.24 (m, 1H), 4.65-4.60 (m, 1H), 4.43-4.37 (m, 1H), 4.07-4.01 (m, 1H), 3.98 (s, 3H), 3.64-3.59 (m, 1H); ^{13}C{H}NMR (100 MHz, $CDCl_3$) δ 167.4, 159.1, 156.3, 148.5, 137.3, 137.0, 134.3, 130.9, 129.1, 128.8, 127.5, 124.2, 124.0, 123.9, 123.8, 122.3, 120.8, 119.0, 110.3, 62.6, 52.4, 47.9; IR (KBr): $\tilde{\nu}$ = 3297, 2919, 1749, 1410, 1265, 1130, 768, 696 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{24}H_{20}N_3O_4$, 414.1454; found: 414.1444.

3-(2,4-diphenyl-7-(pyridin-2-yl)-1H-indol-3-yl)oxazolidin-2-one (**3ah**)

White solid; Yield: 72.7 mg, 84 %; mp: 220-221 ^{o}C; R_f = 0.40 (DCM/PE = 2:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.05 (s, 1H), 8.72 (d, *J* = 4.0 Hz, 1H), 8.07 (d, *J* = 8.4 Hz, 1H), 7.86-7.73 (m, 4H), 7.62-7.39 (m, 8H), 7.25-7.15 (m, 2H), 4.04-3.97 (m, 1H), 3.40-3.29 (m, 2H), 2.91-2.84 (m, 1H); ^{13}C{H}NMR (100 MHz, $CDCl_3$) δ 157.9, 157.3, 148.6, 140.4, 136.8, 136.0, 135.7, 133.7, 131.1, 129.1, 128.9, 128.5, 128.1, 127.5, 127.3, 124.1, 122.0, 121.6, 120.1, 120.0, 119.8, 109.4,

61.9, 48.0; IR (KBr): $\tilde{\nu}$ = 3278, 1751, 1587, 1463, 1404, 1241, 1107, 1040, 767, 699 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{28}H_{22}N_3O_2$, 432.1712; found: 432.1707.

3-(5-chloro-2-phenyl-7-(pyridin-2-yl)-1H-indol-3-yl)oxazolidin-2-one (3ai)

White solid; Yield: 70.3 mg, 90 %; mp: 245-246 ^oC; R_f = 0.38 (DCM/PE = 2:1); ^1H NMR (400 MHz, $CDCl_3$) δ 11.62 (s, 1H), 8.70-8.69 (m, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.82-7.72 (m, 4H), 7.58-7.42 (m, 4H), 7.25-7.23 (m, 1H), 4.53 (t, *J* = 8.0 Hz, 2H), 3.82 (t, *J* = 8.0 Hz, 2H); $^{13}C\{H\}$NMR (100 MHz, $CDCl_3$) δ 158.0, 156.0, 148.7, 136.9, 135.5, 131.5, 130.6, 129.2, 128.8, 127.3, 127.1, 126.2, 122.2, 122.0, 120.4, 120.0, 118.6, 109.6, 62.6, 47.4; IR (KBr): $\tilde{\nu}$ = 3314, 1745, 1590, 1437, 1401, 1123, 1036, 784, 696 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{22}H_{17}ClN_3O_2$, 390.1009; found: 390.1004.

3-(5-bromo-2-phenyl-7-(pyridin-2-yl)-1H-indol-3-yl)oxazolidin-2-one (3aj)

White solid; Yield: 83.3 mg, 96 %; mp: 238-239 ^oC; R_f = 0.35 (PE/EA = 2:1); ^1H NMR (400 MHz, $CDCl_3$) δ 11.65 (s, 1H), 8.72 (d, *J* = 4.0 Hz, 1H), 7.99 (d, *J* = 8.4 Hz, 1H), 7.88 (s, 1H), 7.85-7.81 (m, 1H), 7.75-7.73 (m, 3H), 7.54 (t, *J* = 7.2 Hz, 2H),7.45 (t, *J* = 7.2 Hz, 1H) 7.30-7.28,4.54 (t, *J* = 8.0 Hz, 2H), 3.83 (t, *J* = 8.0 Hz, 2H); $^{13}C\{H\}$NMR (100 MHz, $CDCl_3$) δ 158.0, 156.0, 148.7, 137.0, 135.4, 131.8, 130.6, 129.2, 128.8, 127.9, 127.2, 123.0, 122.4, 122.2, 121.6, 120.1, 113.7, 109.5, 62.6, 47.4; IR (KBr): $\tilde{\nu}$ = 3336, 2921, 1751, 1590, 1481, 1396, 1271, 1121, 758, 694 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{22}H_{17}BrN_3O_2$, 434.0504; found: 434.0499.

3-(6-methyl-2-phenyl-7-(pyridin-2-yl)-1H-indol-3-yl)oxazolidin-2-one (3ak)

White solid; Yield: 45.2 mg, 61 %; mp: 193-194 ^oC; R_f = 0.10 (PE/EA = 2:1); ^1H NMR (400 MHz, $CDCl_3$) δ 9.68 (s, 1H), 8.77 (d, *J* = 4.0 Hz, 1H), 7.84-7.80 (m, 1H), 7.63-7.57 (m, 3H),

7.48-7.42 (m, 3H), 7.38-7.27 (m, 2H), 7.13 (d, J = 8.0 Hz, 1H), 4.49 (t, J = 8.0 Hz, 2H), 3.81 (t, J = 8.0 Hz, 2H), 2.55 (s, 3H); $^{13}C\{H\}$NMR (100 MHz, $CDCl_3$) δ 158.0, 156.9, 149.4, 136.4, 133.8, 133.7, 131.1, 130.1, 129.0, 128.2, 127.0, 125.6, 124.5, 123.8, 122.6, 121.8, 118.2, 110.5, 62.5, 47.5, 20.8; IR (KBr): $\tilde{v}$ = 3057, 2920, 1748, 1604, 1446, 1266, 763, 696 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{23}H_{20}N_3O_2$, 370.1556; found: 370.1550.

3-(6-chloro-2-phenyl-7-(pyridin-2-yl)-1H-indol-3-yl)oxazolidin-2-one (3al)

White solid, Yield: 52.0 mg, 67 %; mp: 226-227 °C; R_f = 0.20 (PE/EA = 2:1); ^1H NMR (400 MHz, $CDCl_3$) δ 10.07 (s, 1H), 8.77 (d, J = 3.2 Hz, 1H), 8.11 (d, J = 8.0 Hz, 1H), 7.86 (t, J = 7.6 Hz, 1H), 7.63 (d, J = 7.6 Hz, 2H), 7.50-7.29 (m, 5H), 4.52 (t, J = 8.0 Hz, 2H), 3.81 (t, J = 8.0 Hz, 2H); $^{13}C\{H\}$NMR (100 MHz, $CDCl_3$) δ 157.9, 154.7, 149.0, 136.5, 135.0, 133.9, 130.5, 129.1, 128.7, 127.1, 126.4, 124.5, 123.3, 122.6, 121.2, 119.1, 110.5, 62.6, 47.3; IR (KBr): $\tilde{v}$ = 3420, 2920, 1749, 1592, 1435, 1264, 1130, 761, 695 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{22}H_{17}ClN_3O_2$, 390.1009; found: 390.1004.

3-(7-(5-methylpyridin-2-yl)-2-phenyl-1H-indol-3-yl)oxazolidin-2-one (3am)

Pale yellow solid; Yield: 68.1 mg, 92 %; mp: 88-89 °C; R_f = 0.33 (PE/EA = 2:1); ^1H NMR (400 MHz, $CDCl_3$) δ 11.67 (s, 1H), 8.51 (s, 1H), 7.86 (d, J = 8.4 Hz, 1H), 7.72 (t, J = 7.6 Hz, 3H), 7.58-7.37 (m, 5H), 7.21 (t, J = 7.6 Hz, 1H), 4.48 (t, J = 8.0 Hz, 2H), 3.80 (t, J = 8.0 Hz, 2H), 2.34 (s, 3H); $^{13}C\{H\}$NMR (100 MHz, $CDCl_3$) δ 158.0, 154.5, 148.7, 137.3, 133.9, 133.0, 131.1, 131.0, 129.1, 128.3, 127.0, 126.2, 121.0, 120.3, 119.9, 119.3, 118.8, 110.0, 62.5, 47.5, 18.1; IR (KBr): $\tilde{v}$ = 3327, 1751, 1602, 1475, 1400, 1253, 1127, 1033, 735, 693 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{23}H_{20}N_3O_2$, 370.1556; found: 370.1550.

3-(7-(5-chloropyridin-2-yl)-2-phenyl-1H-indol-3-yl)oxazolidin-2-one (3an)

White solid, Yield: 72.0 mg, 93 %; mp: 161-162 ^{o}C; R_f = 0.33 (PE/EA = 2:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.34 (s, 1H), 8.66 (d, *J* = 2.4 Hz, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.74-7.73 (m, 4H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 2H), 7.43 (t, *J* = 7.6 Hz, 1H), 7.26-7.22 (m, 1H), 4.52 (t, *J* = 8.0 Hz, 2H), 3.83 (t, *J* = 8.0 Hz, 2H); ^{13}C{H}NMR (100 MHz, $CDCl_3$) δ 158.0, 155.5, 147.4, 136.6, 134.3, 132.8, 130.9, 129.7, 129.2, 128.6, 127.1, 126.4, 120.7, 120.5, 120.5, 119.93, 119.87, 110.3, 62.6, 47.5; IR (KBr): $\tilde{\nu}$ = 3363, 1751, 1463, 1269, 1120, 738, 695 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{22}H_{17}ClN_3O_2$, 390.1009; found: 390.0991.

3-(7-(4-methylpyridin-2-yl)-2-phenyl-1H-indol-3-yl)oxazolidin-2-one (3ao)

White solid; Yield: 43.8 mg, 60 %; mp: 143-144 ^{o}C; R_f = 0.33 (PE/EA = 2:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.74 (s, 1H), 8.56 (d, *J* = 5.2 Hz, 1H), 7.84 (s, 1H), 7.81-7.75 (m, 3H), 7.61 (d, *J* = 7.6 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 2H), 7.43-7.40 (m, 1H), 7.27-7.23 (m, 1H), 7.05 (d, *J* = 4.8 Hz, 1H), 4.52 (t, *J* = 8.0 Hz, 2H), 3.84 (t, *J* = 8.0 Hz, 2H), 2.45 (s, 3H); ^{13}C{H}NMR (100 MHz, $CDCl_3$) δ 158.1, 157.1, 148.3, 147.7, 134.1, 133.3, 131.2, 129.1, 128.4, 127.1, 126.2, 122.7, 121.0, 120.6, 120.3, 120.1, 119.20, 110.0, 62.5, 47.5, 21.4; IR (KBr): $\tilde{\nu}$ = 3460, 1752, 1609, 1276, 1120, 737, 695 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{23}H_{20}N_3O_2$, 370.1556; found: 370.1550.

3-(2-phenyl-7-(pyrimidin-2-yl)-1H-indol-3-yl)oxazolidin-2-one (3ap)

White solid; Yield: 62.0 mg, 87 %; mp: 249-250 ^{o}C; R_f = 0.20 (PE/EA = 2:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.23 (s, 1H), 8.85 (d, *J* = 4.8 Hz, 2H), 8.48 (d, *J* = 7.6 Hz, 1H), 7.77-7.71 (m, 3H), 7.53 (t, *J* = 7.6 Hz, 2H), 7.43 (t, *J* = 7.6 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.19 (t, *J* = 4.8

Hz, 1H), 4.54 (t, *J* = 8.0 Hz, 2H), 3.86 (t, *J* = 8.0 Hz, 2H); $^{13}C\{H\}$NMR (100 MHz, $CDCl_3$) δ 165.0, 158.1, 156.8, 134.1, 133.7, 131.0, 129.2, 128.6, 127.2, 126.2, 123.7, 121.4, 120.6, 120.0, 118.4, 110.5, 62.6, 47.5; IR (KBr): $\tilde{\nu}$ = 3378, 1749, 1570, 1414, 1258, 784, 766, 591 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{21}H_{17}N_4O_2$, 357.1352; found: 357.1341.

Synthesis of JohnphosAu(1a)SbF_6

To a solution of JohnphosAu(MeCN)SbF_6 (0.05 mmol, 39 mg) and ynamide **1a** (0.1 mmol, 18.7 mg) in 3 mL dichloromethane was carefully added 50 mL n-hexane without disturbing the dichloromethane layer. The desired product, JohnphosAu(**1a**)SbF_6, was precipitated out as white crystals in 99 % yield (45.8 mg) over 24 hours at -18 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.88 (m, 1H), 7.72 – 7.70 (m, 2H), 7.53 – 7.51 (m, 2H), 7.36 – 7.35 (m, 3H), 7.25 – 7.21 (m, 1H), 7.15 – 7.08 (m, 4H), 7.04 – 7.01 (m, 1H), 5.68 (t, J = 8.8 Hz, 2H); 4.38 (t, J = 8.8 Hz, 2H), 1.46 (d, $J(^1H-^{31}P)$ = 15.2, 18H), 1.44 (s, 9H); $^{13}C\{H\}$NMR (100 MHz, $CDCl_3$) δ 164.02 (d, $J(^{13}C-^{31}P)$ = 3.3), 159.07 (d, $J(^{13}C-^{31}P)$ = 8.3), 153.66, 152.54, 149.60 (d, $J(^{13}C-^{31}P)$ = 14.3), 143.19, 134.23, 133.14 (d, $J(^{13}C-^{31}P)$ = 7.4), 130.82 (d, $J(^{13}C-^{31}P)$ = 1.7), 129.28, 128.78, 128.60, 128.47, 128.27, 127.18 (d, $J(^{13}C-^{31}P)$ = 6.3), 126.13 (d, $J(^{13}C-^{31}P)$ = 41.2), 124.01, 81.60, 45.09, 37.75 (d, $J(^{13}C-^{31}P)$ = 22.9), 30.93 (d, $J(^{13}C-^{31}P)$ = 6.5); ^{31}P NMR (162 MHz, $CDCl_3$)δ 64.28; IR (KBr) 2958, 1778, 1754, 1734, 1678, 1634, 1474, 1393, 1370, 1175, 1021 cm^{-1}; HRMS-(ESI) (m/z): $(M–SbF_6)^+$ calcd for $C_{31}H_{36}AuNO_2P$, 682.2149; found: 682.2144.

Synthesis of JohnphosAu(2a)SbF_6

A round bottom flask equipped with a magnetic stirrer bar was charged with JohnphosAuCl (0.1mmol, 53.1 mg), $AgSbF_6$ (0.1mmol, 34.3 mg) and DCM (1 mL). The mixture was stirred for 10 minutes at room temperature, and then to this mixture was added pyrido[1,2-b]indazole **2a**

(0.1 mmol, 33.6 mg). After 30 min, the mixture passed through a pad of silica gel using DCM as eluent. The filtrate was collected and evaporated under reduced pressure to afford JohnphosAu(**2a**)SbF_6 as a pale yellow solid (94 mg, 99 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (d, *J* = 6.0 Hz, 1H), 8.35 (d, *J* = 7.2 Hz, 1H), 8.22 (d, *J* = 8.0 Hz, 1H), 7.98-7.94 (m, 1H), 7.89-7.83 (m, 2H), 7.75 (t, *J* = 7.6 Hz, 1H), 7.61-7.59 (m, 2H), 7.46-7.40 (m, 2H), 7.29 (d, *J* = 2.0 Hz, 1H), 7.22 (d, *J* = 6.8 Hz, 2H), 6.74 (t, *J* = 7.6 Hz, 2H), 5.92 (t, *J* = 7.6 Hz, 1H), 1.59 (d, *J* = 16.0 Hz, 18H); ^{13}C{H}NMR (100 MHz, $CDCl_3$) δ 149.1 (d, *J* = 12.2 Hz), 146.8, 143.0 (d, *J* = 6.4 Hz), 136.1 (d, *J* = 1.4 Hz), 133.4 (d, *J* = 3.6 Hz), 133.1 (d, *J* = 7.5 Hz), 131.4, 131.3 (d, *J* = 2.3 Hz), 129.1, 128.5, 128.2, 127.6 (d, *J* = 7.4 Hz), 127.3, 126.5, 124.0 (d, *J* = 49.6 Hz), 122.2, 120.7, 119.8, 118. 7, 115.0 (d, *J* = 1.8 Hz), 112.5, 38.3 (d, *J* = 26.5 Hz), 31.0 (d, *J* = 5.9 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 59.03; IR (KBr) 3676, 2924, 1644, 1472, 757, 660 cm^{-1}; HRMS-(ESI) (m/z): $(M - SbF_6)^+$calcd for $C_{31}H_{35}AuN_2P$, 663.2203; found: 663.2196.

Synthesis of BODYPY-type dye

To a stirred solution of **3aa** (71.1 mg, 0.20 mmol) in toluene (4 mL) was added triethylamine (83 µl, 0.60 mmol), and the solution was stirred for 10 minutes. BF_3•OEt_2 (0.27 mL, 1.00 mmol) was added dropwise, the reaction mixture was heated to 80 ºC for 2 hours and then cooled to room temperature. The yellow solution was quenched with water (2 mL). The organic layer was washed several times with water, dried over Na_2SO_4 and evaporated to dryness under vacuum to give a yellow solid which was purified by flash chromatography on silica gel (PE/EA=1:1), providing a yellow solid (64.5 mg, 80%). ^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ 8.94-8.87 (m, 1H), 8.54 (t, *J* = 8.0 Hz, 1H), 8.32 (d, *J* = 7.6 Hz, 1H), 7.92-7.89 (m, 1H), 7.72 (d, *J* = 7.2 Hz, 1H), 7.58-7.51 (m, 1H), 7.41 (t, *J* = 7.6 Hz, 1H), 4.44 (t, *J* = 8.0 Hz, 1H), 3.77 (t, *J* = 8.0 Hz, 1H);

$^{13}C\{H\}$NMR (100 MHz, $(CD_3)_2SO$) δ 157.8, 149.2, 144.1, 143.4, 140.3, 132.9, 131.6, 129.9, 129.0, 128.7, 125.3, 125.0, 123.5, 121.9, 121.0, 120.4, 114.6, 113.0, 63.0, 47.8; ^{19}F NMR (376 MHz, $(CD_3)_2SO$) δ 126.3; ^{11}B NMR (128 MHz, $(CD_3)_2SO$) δ 2.12; HRMS-(ESI) (m/z): $(M + H)^+$calcd for $C_{22}H_{17}BF_2N_3O_2$, 404.1382; found 404.1376.

ASSOCIATED CONTENT

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Notes

The authors declare no competing financial interests

ACKNOWLEDGMENT

We thank the financial support by NSFC (Grant No. 21402197, 21502190), NSF of Fujian (Grant No. 2015J05043), Hundred-Talent Program and the Strategic Priority Research Program of the Chinese Academy of Sciences (Grant No. XDB20000000). We also thank Prof. Daqiang Yuan for crystallographic analysis of complex JohnphosAu(**1a**)SbF6.

Supporting Information.

The Supporting Information is available free of charge on the ACS Publications website. Mechanistic experiments, kinetic data, ^{1}H and ^{13}C NMR spectra for all described compounds (PDF)

Crystal data of compounds **3aa**, **3ca**, **3ah**, JohnphosAu(**1a**)SbF_6 and JohnphosAu(**2a**)SbF_6 (CIF)[26].

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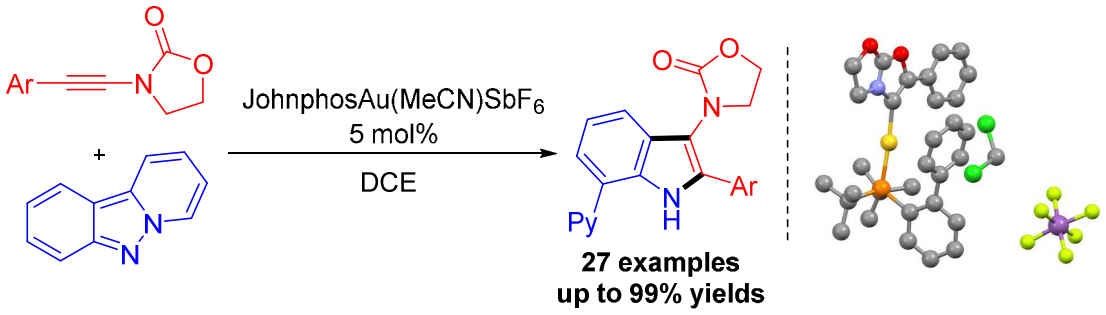
(27) CCDC 1478721 (**3aa**), CCDC 1478722 (**3ca**), CCDC 1478725 (**3ah**), CCDC 1478727 (JohnphosAu(**1a**)SbF_6), CCDC 1478742 (JohnphosAu(**2a**)SbF_6) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.



- β-Regioselective Formal [3+2] Cycloaddition
- 100% Atom Efficiency
- First Isolated Complex of Gold Catalyst with Ynamide
- Mechanistic Studies