Advanced Synthesis & Catalysis

Accepted Article

Title: Gold-catalyzed Oxidative Cross-coupling Reactions Among Two Distinct Arenes and One Gold Carbene with Phosphoric Acids as Cocatalysts

Authors: Rai-Shung Liu, Manoj D. Patil, and Balaji Sopanrao Kale

To be cited as: *Adv. Synth. Catal.* 10.1002/adsc.202000879

Link to VoR: https://doi.org/10.1002/adsc.202000879

10.1002/adsc.202000879

FULL PAPER

DOI: 10.1002/adsc.202((will be filled in by the editorial staff))

Gold-Catalyzed Oxidative Cross-coupling Reactions among Two Distinct Arenes and One Gold Carbene with Phosphoric Acids as Cocatalysts

Manoj D. Patil,[a] Balaji S. Kale,[a] and Rai-Shung Liu[a]*

[a] Frontier Research Center for Matter Science and Technology, Department of Chemistry, National Tsing-Hua University, Hsinchu, Taiwan, ROC
Email: rsliu@mx.nthu.edu.tw

Received: ((will be filled in by the editorial staff))

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201######.((Please delete if not appropriate))

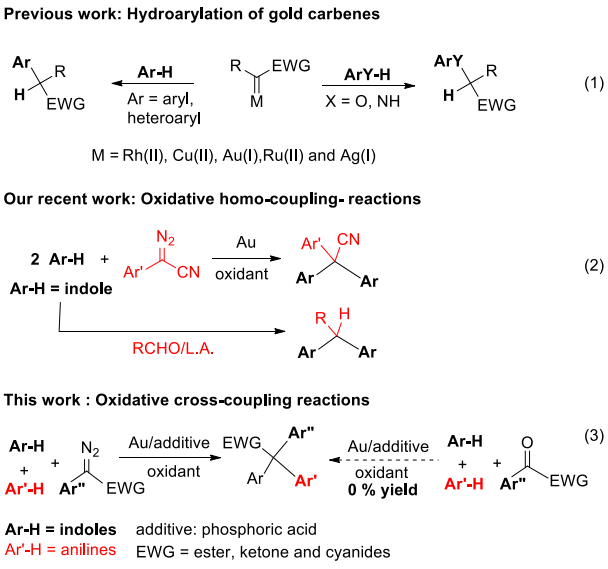
Abstract: Gold-catalyzed oxidative cross-coupling reactions of two distinct arenes with one gold carbene furnish triarylmethane products. Notably, competitive homo-coupling reactions are efficiently suppressed with a phosphoric acid as co-catalyst (10 mol%) in THF. These cross-coupling reactions have a wide scope of applicable substrates, with respect to indoles, arylamines, and *α*-aryl diazo cyanides or esters. Our mechanistic analysis indicates that the basicity of the arylanilines greatly affects the cross-coupling efficiency.

Keywords: gold catalysis; oxidative cross coupling; gold carbenes; α-aryl diazo compounds; indoles; anilines.

Introduction

Metal carbenes are versatile species to react with various nucleophiles to form new C–Y bonds (Y = C, O, N).[1-2] In the presence of phenols, arylamines and electron-rich arenes or heteroarenes, metal carbenes typically afford Y–H insertion products (Y = C, O or N) over various catalysts including Rh, Au, Ag, Ru, Pd or Cu (Equation 1).[3-6] In seeking new carbene reactivity, we developed gold-catalyzed oxidative couplings of two indoles with one *α*-cyano gold carbene to form 2-substituted 2,2-di(indolyl)acetonitriles efficiently (Equation 2).[7] Particularly notable are the dication synthons[8] of gold carbenes to allow a double attack of indole nucleophiles. However, products of this type could be alternatively obtained from Lewis-acid catalyzed condensations of aldehydes with two indoles (Equation 2), thus rendering these oxidative couplings less appealing.

Oxidative cross-coupling of two distinct aryl C–H bonds to form unsymmetric biaryl species is an inspiring topic in metal catalysis.[9] We sought a new strategy to enable a cross-coupling reaction of two distinct arenes with one gold carbene. This task is challenging because competitive homo-coupling reactions must be suppressed efficiently with building



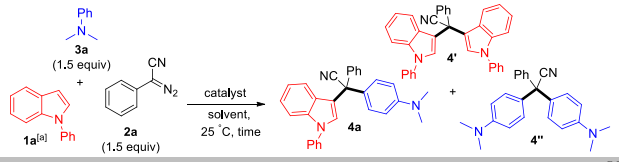
a new strategy. With our efforts, this work describes the first success of catalytic cross-coupling reactions involving one indole, one arylamine and one gold carbene (Equation 3). Our new strategy employs phosphoric acid (10 mol%) in THF to suppress the two homo-coupling reactions as depicted in Equation 3. Notably, our experimental data exclude the

intermediacy of α-cyano aryl ketones that were proved to be inactive under the running conditions (*vide infra*).

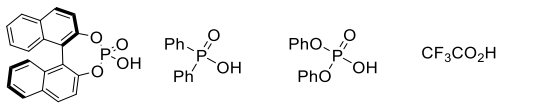
Result and Discussion

Table 1 shows the conditions and catalysts to optimize the efficiency of cross-coupling reactions among indole **1a**, *N*,*N*-dimethyl aniline **3a** and α-phenyldiazo cyanide **2a** in dichloromethane (DCM), aiming at our target **4a**. Among the three phosphine gold catalysts, L'AuCl/AgOTf (L'= P(*t*-Bu)$_2$(o-biphenyl), PPh_3 and $P(OPh)_3$, entries 1-3), triphenyl phosphite was better than the other two phosphine ligands to afford compound **4a** in 26% yield; this was encouraging because the formation of two homo-coupling products **4'** and **4"** was greatly suppressed. We thus increased the loading of AgOTf to 50 mol%, further improving the yield of compound **4a** slightly to 31% (entry 4). The chemoselectivity was greatly improved on changing the solvent from DCM to MeCN, giving compound **4a** in 49% yield (entry 6). We thus sought a suitable Brønsted acid as a co-catalyst because a protodeauration step was presumably involved in the reaction mechanism. As shown in entry 6, the presence of phosphoric acid **A-1** (10 mol%, pK_a 1.14) improved the yield of species **4a** to 58% in MeCN (entry 7), and further to 69% yield in THF (entry 8). We also tested diphenylphosphinic acid **A-2** (pK_a 2.30) and diphenylphosphoric acid **A-3** (pK_a 1.12),[10] which delivered the same product in 62 and 72% yield, respectively (entries 9 and 10). To clarify the effect of the acidity, we employed highly acidic CF_3CO_2H (pK_a = 0.0) to afford the desired product **4a** in a decreased yield ca. 59% (entry 11). Brønsted acid such as **A-3** with a moderate acidity (pK_a = 1.12) is more appropriate for this cross-coupling reaction.

Table 1. Cross-coupling reactions under various conditions



Entry	Catalyst (mol%)	Additive (10 mol%)	Solvent	Time (h)	Yield[b] 4a	4'	4''
1[c]	LAuCl/AgOTf (10/10)	--	DCM	10	17	26	--
2	PPh_3AuCl/AgOTf (10/10)	--	DCM	40	21	15	--
3	$(PhO)_3$PAuCl/AgOTf (10/10)	--	DCM	10	26	09	--
4	$(PhO)_3$PAuCl/AgOTf (10/50)	--	DCM	12	31	11	--
5[d]	AgOTf (50)	--	DCM	20	--	--	--
6	$(PhO)_3$PAuCl/AgOTf (10/50)	--	MeCN	15	49	08	11
7	$(PhO)_3$PAuCl/AgOTf (10/50)	A-1	MeCN	10	58	--	10
8	$(PhO)_3$PAuCl/AgOTf (10/50)	A-1	THF	08	69	--	06
9	$(PhO)_3$PAuCl/AgOTf (10/50)	A-2	THF	09	62	--	10
10	$(PhO)_3$PAuCl/AgOTf (10/50)	A-3	THF	06	72	--	08
11	$(PhO)_3$PAuCl/AgOTf (10/50)	A-4	THF	06	59	--	17
12[e]	--	A-4	THF	24	--	--	--



[a] **1a** = 0.2 M, **2a** = 1.5 equiv., **3a** = 1.5 equiv.

[b] Product yields are obtained after purification from a silica column.

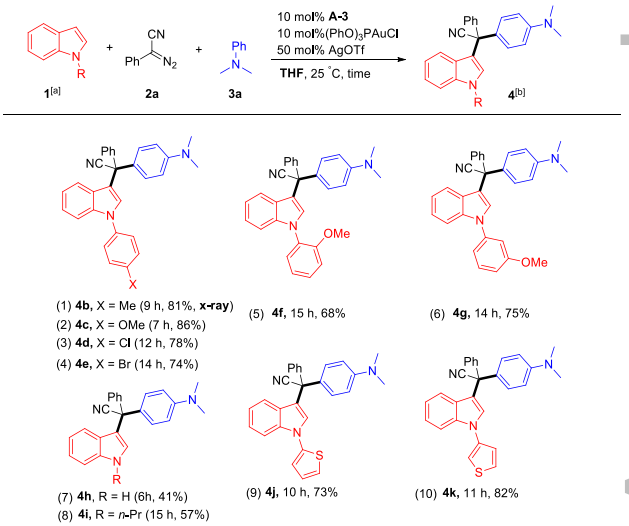
[c] L = P(*t*-Bu)2(*o*-biphenyl).

[d] **3a** was recovered in 69% yield in entry 5.

[e] The amount of **1a** and **3a** recovered was 67 and 75%, respectively.

We tested these cross-coupling reactions on various indole derivatives **1b–k** to assess the generality of the reactions (Table 2). For various *N*-phenyl substituents as in species **1b–e** (X = Me, OMe, Cl and Br), the cross-coupling reactions gave product yields up to 81-86%, for those bearing electron-donating groups such as X = Me (**4b**) and OMe (**4c**), but the yields decreased to 74-78% for X = Cl (**4d**) and Br (**4e**). This trend correlates well with the nucleophilicity of the indoles. The molecular structure of compound **4b** was confirmed by X-ray diffraction.[11] For *N*-*meta* or -*ortho* substituted methoxy indoles **1f** and **1g** their resulting products **4f** and **4g** were obtained in 68 and 75% yield (entries 5 and 6). This reaction also worked well with unsubstituted indole **1h** and *N*-alkyl indole **1i** (R = *n*-Pr), which delivered coupling products **4h** and **4i** in lower yields (41 and 57%, entries 7 and 8). These oxidative coupling reactions were also applicable to 2- or 3-thienyl-containing indoles **1j** and **1k**, rendering compounds **4j** and **4k** in 73 and 82% yield, respectively (entries 9 and 10).

Table 2. Oxidative coupling reactions with various indoles



[a] **1c** = 0.26 M.

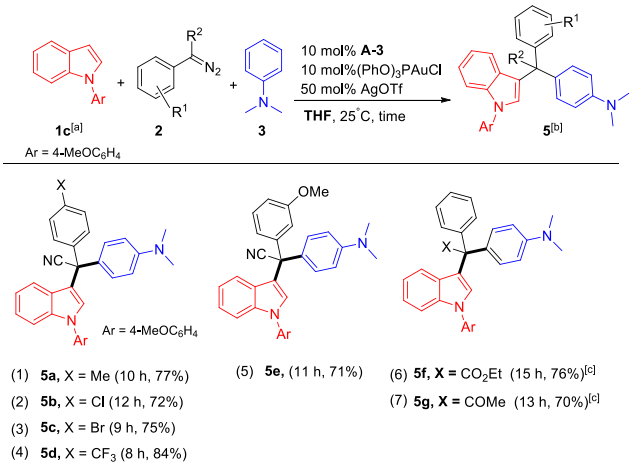
[b] Product yields are obtained after purification from a silica column.

Table 3 depicts the applicability of these cross-coupling reactions to various α-diazo species including cyanides, esters and ketones. For α-phenyldiazo cyanides **2b-2e** bearing *para*-substituents (X = Me, Cl, Br and CF_3), their resulting products **5a-5d** were obtained in 72-84% yields (entries 1-4). For meta-methoxyphenyl analogue **2f,** its corresponding product

10.1002/adsc.202000879

5e was produced in 71% yield (entry 5). We performed the reactions on *α*-diazo ester **2g** and ketone **2h** which afforded cross-coupling products **5f** and **5g** in 76 and 70% yield, respectively (entries 6 and 7).

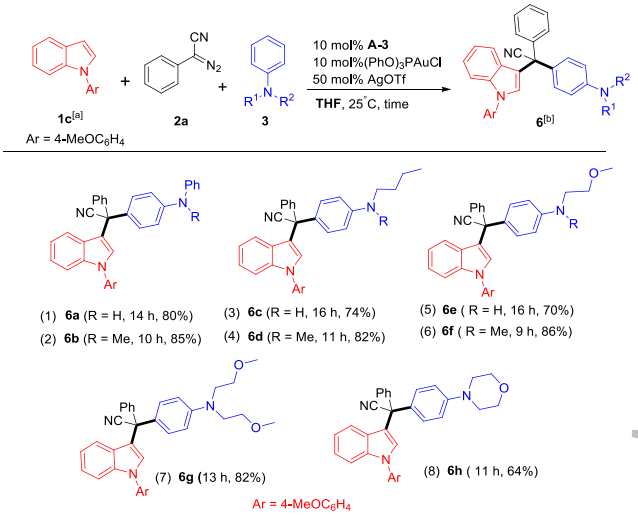
Table 3. Cross-coupling reactions with α-diazo species



[a] **1c** = 0.18 M.
[b] Product yields are obtained after purification from a silica column.
[c] Reactions were carried out at 50 °C.

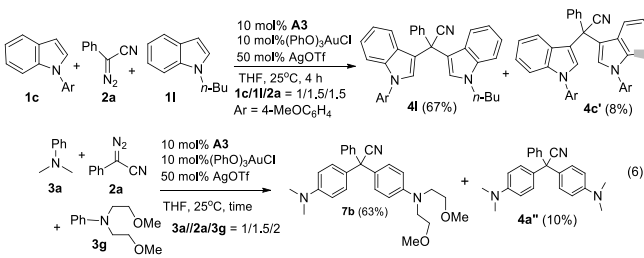
In Table 4, we prepared various *N*-substituted anilines **3b**-**3i** to assess the effects of amine functionalities. We first performed the reactions on *N*-phenyl substituted anilines **3b** (R = H) and **3c** (R = Me), yielding the cross-coupling products **6a** and **6b** in 80 and 85% yield, respectively (entries 1 and 2). For electron-rich *N*-butyl-derived anilines **3d** and **3e**, their resulting products **6c** and **6d** were obtained in 74 and 82% yield, respectively (entries 3 and 4). Again, for anilines **3f** and **3g** bearing a *N*-(2-methoxyethyl) substituent, we obtained a yield for *N*- methyl product **6f** (R = Me, 86%), better than that (70%) of compound **6e (**R = H entries 5 and 6). For anilines **3h** and **3i** bearing less basic *N*-bis(2-methoxyethyl) and morpholine**,** their corresponding products **6g** and **6h** were obtained in 82 and 64% yield, respectively (entries 7 and 8). With these results, we observed efficiency for R = Me as in entries 2,4,6 greater than for their unsubstituted anilines R = H (entries 1, 3, 5). A basic aniline is expected to diminish the activity of the gold catalyst when gold is coordinated with aniline; this positive effect might arise from an increased nucleophilicity of a basic aniline. According to our subsequent study, a deprotonation of a basic aniline seems to be more important to enhance this cross-coupling efficiency (*vide infra*).

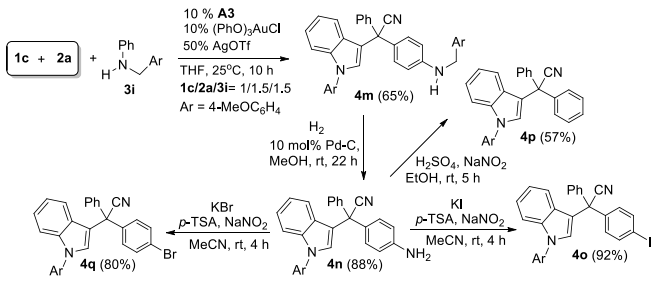
Table 4. Cross-coupling reactions with various anilines



[a] **1c** = 0.18 M.
[b] Product yields are obtained after purification from a silica column.

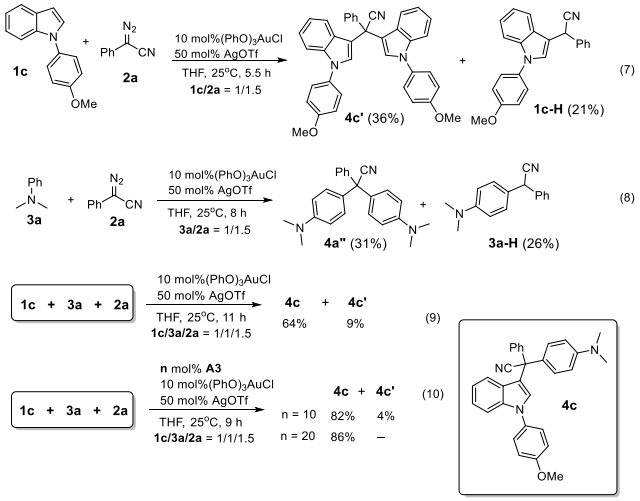
We also achieved catalytic cross-coupling reactions between two distinct indoles and one carbene (Equation 5). Under the standard conditions (molar ratio: **1c**/**1l**/**2a** = 1/1.5/1.5), we obtained desired product **4l** from a cross-coupling reaction, in addition to compound **4c'** in a minor proportion. We also managed to achieve the cross-coupling reactions among two distinct anilines and one carbene; the result is depicted in Equation 6. Under the conditions **3a**/**3g** /**2a** = 1/2.0/1.5, we obtained the resulting cross-coupling products **7b** in 63% yields. This good yield was attributed to a large loading (2 equiv) of anilines **3g**, that has moderate nucleophilicity.



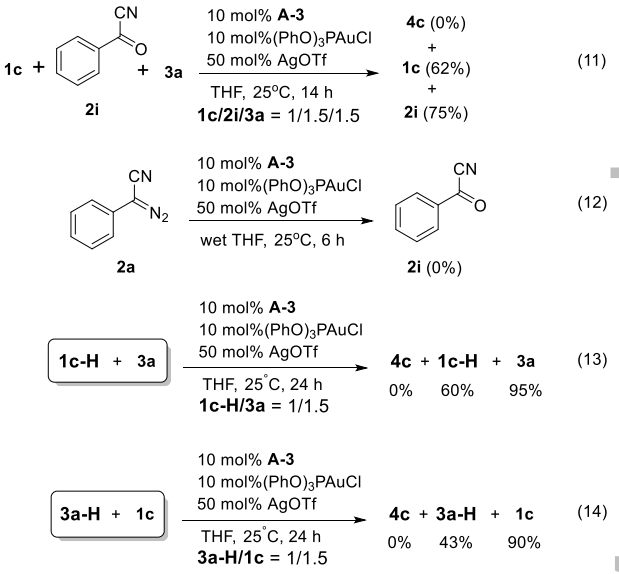


Scheme 1. Chemical functionalizations of cross-coupling products

We performed chemical transformations of one cross-coupling product **4m** into other indole/arene/carbene species that could not be obtained in this catalysis. We prepared *N*-benzyl derivative **4m** in 65% yield according to our protocol (Scheme 1). Reductive debenzylation of species **4m** with Pd/C/H_2 in MeOH yielded compound **4n** in 88% yield.[12] Treatment of species **4n** with *p*-TSA/$NaNO_2$ yielded a diazonium salt that reacted with KI to form 4-iodophenyl product **4o** in 92% yield.[13a] With this diazonium species, compound **4n** was further transformed into an unsubstituted phenyl derivative **4p** and 4-bromophenyl product **4q** in 57 and 80% yield, respectively.[13b] Accordingly, various indole/arene/carbene coupling products can be derived from chemical functionalization of their aniline derivative **4m**, further expanding the scope of applications.

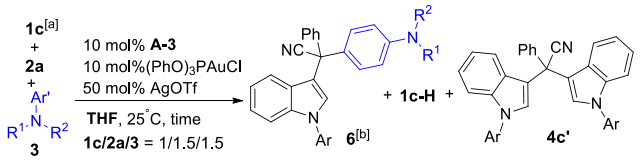


We performed two control experiments (Equations 7 and 8) to examine the relative rates of reaction of indole **1c** versus aniline **3a** toward gold carbenes. Under the same conditions, an equimolar mixture of **1c**/**2a** and **3a**/**2a** gave rise to homo-coupling and hydroarylation products **4c'**/**1c-H** and **4a"**/**3a-H**; their respective yields were 36 and 31% for species **4c'** and **1c-H,** and 31 and 26% for species **4a"** and **3a-H**. According to the duration (5.5 h versus 8 h) of reaction, indole **1c** is superior to aniline **3a** as a nucleophile; this assessment is evident also with preferable formation of homo-coupling indole product **4'** in Table 1. Notably, when aniline **1c** was present in the indole/diazo mixture, formation of these four major products **4c'**/**1c-H** and **4a"**/**3a-H** in Equations 5 and 6 became so seriously suppressed such that cross-coupling product **4c** was obtained up to 64% yield (Equation 9). When phosphoric acid **A-3** (10 mol%) was present, this **1c/2a/3a** mixture generated desired **4c** up to 82% yield, further to 86% with acid **A-3** at a 20 mol% loading (Equation 10).



To clarify the role of α-cyano ketones as viable intermediates, we prepared an authentic ketone **2i** that turned out to be robust under the operating conditions, with a large recovery of all starting materials (Equation 11). In fact, α-cyano diazo **2a** could not be converted into acyl cyanide **2i** with Au(I) and Ag(I) in wet THF solution (Equation 12). Accordingly, addition of arenes at gold carbenes is confirmed to be an initial step. We performed two new experiments that show that hydroarylation products **1c-H** and **3c-H** are inactive species in this cross-coupling process. The reactions of **1c-H** with **3a** and **3a-H** with **1c** failed to give the desired cross-coupling product **4c** (Equations 13 and 14).

Our next task was to clarify the basicity of anilines in the cross-coupling reaction. As shown in Scheme 2, we examined the reactions with less basic anilines **3j** ($R^1 = R^2 = H$) and **3k** ($R^1 = H$, $R^2 = Ac$), which showed no catalytic activity for either cross- or homo-coupling reactions (entries 1 and 2). We next tested the reaction of *N*, *N*-dimethyl 2,6-dimethylaniline **3l** that turned out to be an ineffective substrate, but we isolated homo-coupling bis(indole) product **4c'** (entry 3). Aniline **3l** is highly hindered for a deprotonation reaction, but not for a *para*-arylation; the high reactivity of a basic aniline in the cross coupling is likely to be associated with a deprotonation.



Entry	3	Ar	R^1	R^2	time (h)	yield (%) 6	1c-H	1c	3	4c'
1	**3j**	Ph	H	H	05	--	–	100	85	–
2	**3k**	Ph	H	Ac	14	--	12	50	95	–
3	**3l**	2,6-Me_2Ph	Me	Me	10	--	–	–	90	67

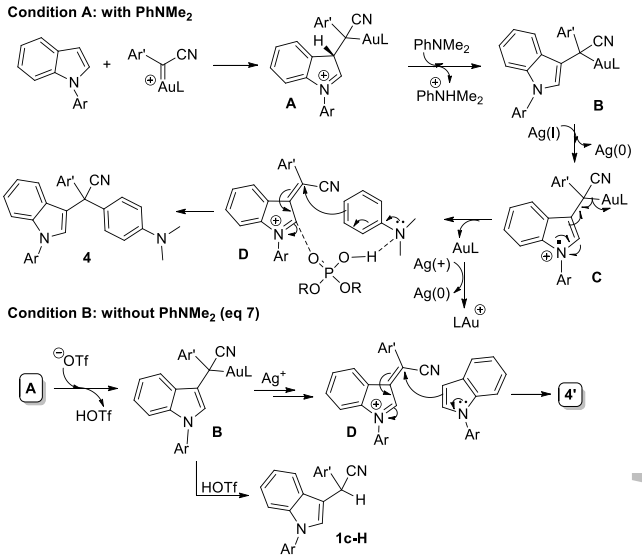
[a] **1c** = 0.18 M

[b] Product yield are obtained after purification from a silica column.

Scheme 2. The role of anilines in cross-coupling reactions

According to our product analysis in Scheme 2, cross-coupling reactions are operable only with those anilines bearing sufficient basicity to enable a deprotonation. Concurrently, phosphoric acid **A-3** also enhanced the efficiency of cross coupling, but its absence still yielded desired product **4c** in 64% yield (Equation 9). We postulate a mechanism involving phosphoric acid **A-3**, as depicted in conditions A **(**Scheme 3). *N*-aryl indoles **2** are obviously more active than those *N*-alkyl anilines to attack gold carbenes to form gold-containing iminium **A**, of which the acidic proton was deprotonated with aniline **2a** to form gold-containing indole **B**. Intermediate **B** is further oxidized by Ag(I) to form radical cation **C**, in which the cationic center induces a dissociation of LAu^+ to generate the indolium species **D** and LAu(0); the latter is quickly oxidized by Ag(I) or other oxidant to regenerate LAu^+. After this transformation **C→D**, the phosphoric acid reacts further with $PhNMe_2$ to form a complex pair. This acid-base pair bears a basic P=O oxygen which can be tightly bound to an iminium salt **D** through an electrostatic interaction to facilitate the cross-coupling reaction. According to our results in Equation 7, in the absence of $PhNMe_2$ (conditions **B**), triflate ion abstracts the acidic proton of **A** to form gold-containing indole **B** and triflic acid. Intermediate **B** can further be oxidized by excessive Ag(I) to form indolium **D** which is attacked by another molecule of indole to get homo-coupling product **4'**. Protodeauration of **B** can also occur with triflic acid to produce the hydroarylation product **1c-H**.

This mechanism rationalizes well the importance of the basicity of anilines to affect the cross-coupling reaction; basic anilines form a tight complex with phosphoric acid in addition to their strong nucleophilicity. For various Brønsted acids (Table 1, entries 8-11), CF_3CO_2H (pK_a 0.0) is inferior to phosphoric acid **A-3** (pK_a 1.12) in this cross coupling because the less basic $CF_3CO_2^-$ anion is not tightly bound to an iminium species **C**.



Scheme 3. A postulated mechanism

Conclusion

Before this work, electron-rich arenes were well known to undergo hydroarylations with gold, rhodium and other carbenes.[2,3] To seek new carbene chemistry, we have developed oxidative cross-coupling reactions between two distinct arenes with one gold carbene over a wide scope of substrates. Our mechanistic analysis indicates that relatively basic arylamines and an additional phosphoric acid are crucial to enhance these cross-coupling reactions, thus providing mechanistic insight into the reactions.

Experimental Section

Synthesis of 2-(4-(dimethylamino) phenyl)-2-phenyl-2-(1-phenyl-1H-indol-3-yl)acetonitrile phenylacetonitrile (4a):

A reaction tube was charged with (chlorotriphenoxyphosphoranyl)gold(I) (28 mg, 0.052 mmol), diphenyl hydrogen phosphate **A-3** (13 mg, 0.052 mmol) and silver(I) trifluoromethanesulfonate (AgOTf) (66 mg, 0.22 mmol). To the above mixture was added a dry THF (1.0 mL), and the mixture was stirred at room temperature under a nitrogen atmosphere for 5 min. To this solution was added a dry THF solution (2 mL) of *N*-phenyl Indole **1a** (100 mg, 0.52 mmol), 2-diazo-2-phenylacetonitrile **2a** (88 mg, 0.77 mmol) and *N*, *N*-dimethyl aniline **3a** (94 mg, 0.77 mmol) with syringe in a period of 25 minute. The mixture was kept stirring at 25 °C for 6 h before it was filtered over a short celite bed. The solvent was concentrated, and the crude product was chromatographed through a silica gel column using ethyl acetate/hexane (10:90) as the eluent to afford compound **4a** (159 mg, 0.37 mmol, 72% yield) as light yellow semi-solid.

2-phenyl-2,2-bis(1-phenyl-1H-indol-3-yl)acetonitrile (4'):

colorless liquid, ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.62 -7.58 (m, 2 H), 7.53 (d, *J* = 8.2 Hz, 2 H), 7.46-7.43 (m, 4 H), 7.40 -7.36 (m, 5 H), 7.33 -7.28 (m, 6 H), 7.22 -7.21 (m, 2 H), 7.11 (td, *J* = 8.0, 0.9 Hz, 2 H), 6.58 (s, 2 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 139.1, 136.9, 131.1, 129.5, 129.3, 128.6, 128.1,

127.8, 126.8, 124.5, 123.0, 121.4, 121.0, 120.8, 116.7, 116.2, 110.8, 44.8; HRMS-ESI+ calcd for $C_{36}H_{25}N_3Na$ (M+H): 522.1946, found: 522.1931.

2,2-bis(4-(dimethylamino)phenyl)-2-phenylacetonitrile (4''):

yellow solid; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.31-7.26 (m, 3 H), 7.24-7.23 (m, 2 H), 7.03 (d, *J* = 8.6 Hz, 4 H), 6.63 (d, *J* = 8.8 Hz, 4 H), 2.93 (s, 12 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 149.8, 141.6, 129.4, 128.7, 128.3, 128.3, 127.5, 124.2, 111.9, 55.8, 40.3; ESI-MS calcd. for $C_{24}H_{25}N_3Na$ (M+Na): 378.1946; Found: 378.1947.

2-(4-(dimethylamino)phenyl)-2-phenylacetonitrile (3a-H):

colorless liquid, 50.44 mg, 26%; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.33-7.26 (m, 5 H), 7.15 (d, *J* = 8.5 Hz, 2 H), 6.66 (d, *J* = 8.7 Hz, 2 H), 5.03 (s, 1 H), 2.92 (s, 6 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 150.2, 136.7, 129.0, 128.4, 127.8, 127.5, 123.2, 120.2, 112.6, 41.7, 40.3; EI-MS calcd. for $C_{16}H_{16}N_2$ (M+): 236.1313; Found: 236.1308.

2-(1-(4-methoxyphenyl)-1H-indol-3-yl)-2-phenylacetonitrile (1c-H):

colorless liquid, 31.8 mg, 21%; ^{1}H NMR (400 MHz, CDCl3): δ 7.50-7.47 (m, 3 H), 7.41 (d, *J* = 8.2 Hz, 2 H), 7.39-7.30 (m, 4 H), 7.23-7.19 (m, 2 H), 7.12 (t, *J* = 7.9 Hz, 1 H), 7.01 (dd, *J* = 6.8, 2.1 Hz, 2 H), 5.42 (s, 1 H), 3.85 (s, 3 H); ^{13}C NMR (100 MHz, CDCl3): δ 158.6, 137.1, 135.3, 132.0, 129.1, 128.2, 127.7, 127.6, 127.2, 126.1, 123.0, 120.6, 119.7, 119.0, 114.8, 111.2, 110.8, 55.6, 34.4; EI-MS calcd. for $C_{23}H_{18}N_2O$ (M+): 338.1419; Found: 338.1416.

2,2-bis(1-(4-methoxyphenyl)-1H-indol-3-yl)-2-phenylacetonitrile (4c'):

colorless semi-solid, 90.2 mg, 36%; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.63 (dd, *J* = 8.5, 1.3 Hz, 2 H), 7.59 (dd, *J* = 7.2, 0.9 Hz, 2 H), 7.36-7.29 (m, 7 H), 7.19-7.14 (m, 4 H), 7.07 (td, *J* = 8.0, 1.2 Hz, 2 H), 7.02-6.99 (m, 4 H), 6.81 (s, 2 H), 3.68 (s, 6 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 154.4, 139.5, 137.9, 130.2, 128.7, 128.4, 128.0, 128.0, 127.8, 127.6, 125.8, 122.3, 120.7, 120.1, 115.2, 112.3, 111.0, 55.6, 44.9; ESI-MS calcd. for $C_{38}H_{29}N_3NaO_2$ (M+Na): 582.2157; Found: 582.2150.

2-(4-(dimethylamino)phenyl)-2-phenyl-2-(1-phenyl-1H-indol-3-yl)acetonitrile (4a):

yellow semi-sold, 159.2 mg, 72%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, *J* = 8.2 Hz, 1 H), 7.47 (d, *J* = 8.2 Hz, 2 H), 7.41-7.37 (m, 6 H), 7.35-7.28 (m, 4 H), 7.24-7.22 (m, 2 H), 7.09 (t, *J* = 7.3 Hz, 1 H), 6.65 (d, *J* = 8.8 Hz, 2 H), 6.60 (s, 1 H), 2.94 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.9, 140.3, 139.2, 137.0, 129.6, 128.9, 128.5, 128.1, 127.8, 126.9, 126.8, 126.6, 124.5, 123.9, 123.0, 122.7, 121.2, 120.7, 117.9, 112.0, 112.0, 110.7, 50.3, 40.3; HRMS-ESI+ calcd for $C_{30}H_{25}N_3Na$ (M+Na): 450.1946, found: 450.1935.

2-(4-(dimethylamino)phenyl)-2-phenyl-2-(1-(p-tolyl)-1H-indol-3-yl)acetonitrile (4b):

yellow solid, 172.6 mg, 81%; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.47 (d, *J* = 8.5 Hz, 1 H), 7.42 (d, *J* = 7.5 Hz, 2 H), 7.37 (d, *J* = 8.1 Hz, 1 H), 7.33 (t, *J* = 7.7 Hz, 2 H), 7.30-7.28 (m, 2 H), 7.27-7.23 (m, 3 H), 7.22 (d, *J* = 9.0 Hz, 2 H), 7.19 (t, *J* = 6.9 Hz, 1 H), 7.06 (t, *J* = 6.9 Hz, 1 H), 6.65 (d, *J* = 8.5 Hz, 2 H) 6.57 (s, 1 H), 2.93 (s, 6 H), 2.38 (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 149.8, 140.3, 137.1, 136.7, 136.6, 130.1, 129.1, 128.9, 128.5, 128.1, 127.7, 126.9, 126.4, 124.5, 122.8, 122.7,, 121.1, 120.5, 117.5, 112.0, 111.7, 50.3, 40.3, 21.0; HRMS-ESI+ calcd for $C_{31}H_{27}N_3Na$ (M+Na): 464.2103, found: 464.2118.

2-(4-(dimethylamino)phenyl)-2-(1-(4-methoxyphenyl)-1H-indol-3-yl)-2-phenylacetonitrile (4c):

yellow semi-solid, 176.2 mg, 86%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43-7.37 (m, 3 H), 7.35-7.28 (m, 5 H), 7.22- 7.19 (m, 3 H), 7.05 (t, *J* = 7.9 Hz, 1 H), 6.96 (d, *J* = 8.9 Hz, 2 H), 6.65 (d, *J* = 8.9 Hz, 2 H), 6.53 (s, 1 H), 3.83 (s, 3 H), 2.93 (s, 6 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 158.6, 149.9, 140.5, 137.7, 132.3, 129.3, 129.0, 128.5, 128.2, 127.7, 126.4, 126.2, 122.8, 122.7, 121.1, 120.5, 117.4, 114.8, 112.2, 110.6, 55.6, 40.3; ESI-MS calcd. for $C_{31}H_{27}N_3NaO$ (M+Na): 480.2052; Found: 480.2038.

2-(1-(4-chlorophenyl)-1H-indol-3-yl)-2-(4-(dimethylamino)phenyl)-2-phenylacetonitrile (4d):

yellow solid, 158.2 mg, 78%; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.45 (d, *J* = 8.0 Hz, 1 H), 7.43-7.40 (m, 3 H), 7.37 (d, *J* = 8.0 Hz, 1 H), 7.34-7.29 (m, 5 H), 7.23-7.18 (m, 4 H), 7.08 (t, *J* = 8.0 Hz, 1 H), 6.65 (d, *J* = 8.8 Hz, 2 H), 6.56 (s, 1 H), 2.93 (s, 6 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 149.8, 140.1, 137.7, 136.9, 132.4, 129.8, 129.7, 128.9, 128.6, 128.5, 128.1, 127.8, 126.7, 125.7, 125.5, 123.2, 122.5, 121.3, 121.0, 120.1, 118.5, 112.0, 110.4, 50.3, 40.3; ESI-MS calcd. for $C_{30}H_{25}ClN_3$ (M+H): 462.1737; Found: 462.1735.

2-(1-(4-bromophenyl)-1H-indol-3-yl)-2-(4-(dimethylamino)phenyl)-2-phenylacetonitrile (4e):

yellow solid, 137.7 mg, 74%; ^{1}H NMR (700 MHz, $CDCl_3$): δ 7.45 (d, *J* = 8.3 Hz, 1 H), 7.43-7.40 (m, 4 H), 7.37 (d, *J* = 8.0 Hz, 1 H), 7.34-7.20 (m, 5 H), 7.24-7.19 (m, 3 H), 7.08 (t, *J* = 7.4 Hz, 1 H), 6.65 (d, *J* = 8.3 Hz, 2 H), 6.56 (s, 1 H), 2.93 (s, 6 H); ^{13}C NMR (175 MHz, $CDCl_3$): δ 149.9, 140.1, 137.6, 136.9, 132.3, 129.7, 128.9, 128.6, 128.5, 128.1, 127.8, 126.7, 126.6, 125.7, 123.2, 122.5, 121.3, 121.0, 118.4, 112.0, 110.4, 50.3, 40.3; ESI-MS calcd. for $C_{30}H_{24}BrN_3Na$ (M+Na): 528.1051; Found: 528.1057.

2-(4-(dimethylamino)phenyl)-2-(1-(2-methoxyphenyl)-1H-indol-3-yl)-2-phenylacetonitrile (4f):

yellow solid, 139.4 mg, 68%; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.43 (d, *J* = 7.2 Hz, 2 H), 7.37 (d, *J* = 8.0 Hz, 1 H), 7.34-7.28 (m, 4 H), 7.23 (d, *J* = 8.5 Hz, 2 H), 7.15 (d, *J* = 4.0 Hz, 2 H), 7.05-7.00 (m, 4 H), 6.65 (d, *J* = 8.9 Hz, 2 H) 6.52 (s, 1 H), 3.72 (s, 3 H), 2.92 (s, 6 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ154.3, 149.8, 140.5, 137.9, 130.4, 128.9, 128.8, 128.4, 128.2, 128.1, 127.6, 127.6, 127.1, 125.9, 122.8, 122.4 120.7, 120.7, 120.2, 116.7, 112.3, 112.0, 111.1, 55.6, 50.3, 40.3; ESI-MS calcd. for $C_{31}H_{27}N_3NaO$ (M+Na): 476.1713; Found: 476.1724.

2-(4-(dimethylamino)phenyl)-2-(1-(3-methoxyphenyl)-1H-indol-3-yl)-2-phenylacetonitrile (4f):

yellow solid, 153.7 mg, 75%; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.54 (d, *J* = 8.4 Hz, 1 H), 7.42 (d, *J* = 7.0 Hz, 2 H), 7.38-7.29 (m, 5 H), 7.22-7.20 (m, 3 H), 7.08 (t, *J* = 7.4 Hz, 1 H), 6.98 (dd, *J* = 6.0, 1.2 Hz, 1 H), 6.94 (t, *J* = 2.1 Hz, 1 H), 6.86 (dd, *J* = 8.0, 2.3 Hz, 1 H), 6.65 (dd, *J* = 6.9, 2.2 Hz, 2 H), 6.60 (s, 1 H), 3.82 (s, 3 H), 2.93 (s, 6 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 160.4, 149.8, 140.2, 140.2, 136.127.8, 9, 130.3, 128.9, 128.5, 128.1, 126.8, 126.6, 123.0, 122.6, 121.2, 120.7, 117.9, 116.7, 112.1, 112.0, 110.8, 110.5, 55.5, 50.3, 40.3; ESI-MS calcd. for $C_{31}H_{27}N_3NaO$ (M+Na): 476.1713; Found: 476.1715.

2-(4-(dimethylamino)phenyl)-2-(1H-indol-3-yl)-2-phenylacetonitrile (4h):

colorless semi-solid, 122.9 mg, 41%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (bs, 1 H), 7.38-7.32 (m, 3 H), 7.31-7.26 (m, 3 H), 7.21-7.15 (m, 3 H), 7.06-7.00 (m, 2 H), 6.64 (d, *J* = 8.5 Hz, 2 H), 6.48 (d, *J* = 2.5 Hz, 1 H), 2.93 (s, 6 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 149.8, 140.4, 136.8, 129.1,

128.9, 128.7, 128.4, 128.1, 127.7, 127.0, 125.4, 122.7, 122.6, 120.7, 120.2, 117.0, 111.9, 111.2, 50.2, 40.3; EI-MS calcd. for $C_{24}H_{21}N_3$ (M+): 351.1735; Found: 351.1738.

2-(4-(dimethylamino)phenyl)-2-phenyl-2-(1-propyl-1H-indol-3-yl)acetonitrile (4i):

yellow semi-solid, 140.8 mg, 57%; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.37-7.35 (m, 2 H), 7.32-7.28 (m, 5 H), 7.20-7.15 (m, 3 H), 6.99 (t, *J* = 7.9 Hz, 1 H), 6.64 (d, *J* = 8.9 Hz, 2 H), 6.38 (s, 1 H), 3.96 (t, *J* = 7.1 Hz, 3 H), 2.93 (s, 6 H), 1.81-1.75 (m, 2 H), 0.86 (t, *J* = 7.3 Hz, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 149.8, 140.7, 137.1, 128.9, 128.4, 128.1, 127.6, 127.4, 126.0, 122.9, 122.0, 120.9, 119.6, 115.1, 112.0, 109.6, 50.3, 48.1, 40.3, 23.4, 11.4; ESI-MS calcd. for $C_{27}H_{27}N_3Na$ (M+Na): 416.2103; Found: 416.2119.

2-(4-(dimethylamino)phenyl)-2-phenyl-2-(1-(thiophen-2-yl)-1H-indol-3-yl)acetonitrile (4j):

yellow semisolid, 158.8 mg, 73%; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.51 (d, *J* = 8.2 Hz, 1 H), 7.42-7.41 (m, 2 H), 7.39 (dd, *J* = 5.2, 1.9 Hz, 1 H), 7.36 (d, *J* = 8.2 Hz, 2 H), 7.34-7.30 (m, 3 H), 7.23-7.20 (m, 4 H), 7.08 (td, *J* = 8.0, 0.8 Hz, 1 H), 6.65 (d, *J* = 9.0 Hz, 2 H), 6.58 (s, 1 H), 2.94 (s, 6 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 149.9, 140.2, 137.7, 137.2, 129.0, 128.9, 125.5, 128.1, 127.8, 126.8, 126.3, 126.1, 123.8, 123.1, 122.6, 121.1, 120.8, 117.7, 115.6, 112.0, 111.8, 50.3, 40.3; ESI-MS calcd. for $C_{28}H_{24}N_3S$ (M+H): 434.1691; Found: 434.1690.

2-(4-(dimethylamino)phenyl)-2-phenyl-2-(1-(thiophen-3-yl)-1H-indol-3-yl)acetonitrile (4k):

yellow semisolid, 178.3 mg, 82%; ^{1}H NMR (700 MHz, $CDCl_3$): δ 7.52 (d, *J* = 8.2 Hz, 1 H), 7.42 (d, *J* = 7.5 Hz, 2 H), 7.41-7.36 (m, 2 H), 7.35-7.29 (m, 5 H), 7.24-7.21 (m, 2 H), 7.19 (d, *J* = 4.8 Hz, 1 H), 7.08 (t, *J* = 7.5 Hz, 1 H), 6.66 (d, *J* = 8.8 Hz, 2 H), 6.59 (s, 1 H), 2.94 (s, 6 H); ^{13}C NMR (175 MHz, $CDCl_3$): δ 151.3, 141.6, 139.2, 138.7, 132.5, 130.8, 130.3, 129.9, 129.5, 129.2, 128.2, 127.7, 127.6, 125.2, 124.5, 122.6, 122.2, 119.1, 117.1, 113.4, 112.2, 51.7, 47.7 ESI-MS calcd. for $C_{28}H_{23}N_3NaS$ (M+Na): 457.1510; Found: 457.1574.

2-(4-(dimethylamino)phenyl)-2-phenyl-2-(1-(thiophen-3-yl)-1H-indol-3-yl)acetonitrile (4k):

yellow semisolid, 152.9 mg, 67%; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.55 (d, *J* = 8.4 Hz, 2 H), 7.51 (d, *J* = 7.9 Hz, 1 H), 7.42 (d, *J* = 8.3 Hz, 1 H), 7.35-7.31 (m, 4 H), 7.29 (dd, *J* = 6.6, 2.1 Hz, 2 H), 7.19 (t, *J* = 8.2 Hz, 2 H), 7.06 (td, *J* = 7.9, 0.9 Hz, 1 H), 7.02 (t, *J* = 7.2 Hz, 1 H), 6.95 (dd, *J* = 6.7, 2.2 Hz, 2 H), 6.72 (s, 1 H), 6.64 (s, 1 H), 4.02-3.99 (m, 2 H), 3.82 (s, 3 H), 1.75-1.70 (m, 2 H), 1.28-1.24 (m, 2 H), 0.88 (t, *J* = 7.3 Hz, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 158.4, 139.5, 137.4, 136.9, 132.1, 128.7, 128.5, 127.8, 126.2, 126.1, 125.8, 122.7, 121.9, 121.7, 121.0, 120.8, 120.3, 119.6, 116.1, 114.6, 113.5, 110.6, 109.5, 55.5, 46.2, 44.8, 32.2, 20.0, 13.6; ESI-MS calcd. for $C_{35}H_{31}N_3NaO$ (M+Na): 532.2365; Found: 532.2378.

2-(4-(dimethylamino)phenyl)-2-(1-(4-methoxyphenyl)-1H-indol-3-yl)-2-(p-tolyl)acetonitrile (5a):

colorless semi-solid, 162.6 mg, 77%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (t, *J* = 6.2 Hz, 2 H), 7.29 (t, *J* = 7.6 Hz, 4 H), 7.23-7.16 (m, 4 H), 7.12 (d, *J* = 7.6 Hz, 2 H), 7.05 (t, *J* = 7.5 Hz, 1 H), 6.96 (d, *J* = 7.3 Hz, 2 H), 6.65 (d, *J* = 7.8 Hz, 2 H), 6.54 (s, 1H), 3.83 (s, 3 H), 2.93 (s, 6 H), 2.32 (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 158.4, 149.8, 137.4, 137.4, 132.1, 129.8. 129.2.129.1, 128.9, 128.0, 127.3, 126.3, 126.1, 125.5, 122.8, 122.7, 121.1, 120.4, 117.4, 114.6, 112.0, 110.5, 55.5, 50.0, 40.3, 21.0; ESI-MS calcd. for $C_{32}H_{30}N_3O$ (M+H): 472.2389; Found: 472.2388.

2-(4-chlorophenyl)-2-(4-(dimethylamino)phenyl)-2-(1-(4-methoxyphenyl)-1H-indol-3-yl)acetonitrile (5b):

colorless solid, 158.6 mg, 72%; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.40 (d, *J* = 8.1 Hz, 1 H), 7.36-7.35 (m, 3 H), 7.31-7.29 (m, 5 H), 7.21-7.19 (m, 2 H), 7.07 (t, *J* = 7.1 Hz, 1 H), 6.97 (d, *J* = 8.8 Hz, 2 H), 6.65 (d, *J* = 8.6 Hz, 2 H), 6.54 (s, 1H), 3.83 (s, 3 H), 2.93 (s, 6 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 158.5, 149.9, 139.0, 137.5, 133.8, 131.9, 129.5, 129.2, 128.8, 128.6, 126.1, 126.0, 122.9, 122.3, 120.9, 120.6, 116.7, 114.8, 114.7, 112.0, 110.7, 55.5, 49.9, 40.3; ESI-MS calcd. for $C_{31}H_{27}ClN_3O$ (M+H): 492.1843; Found: 492.1842.

2-(4-bromophenyl)-2-(4-(dimethylamino)phenyl)-2-(1-(4-methoxyphenyl)-1H-indol-3-yl)acetonitrile (5c):

colorless solid, 180.2 mg, 75%; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.45 (d, *J* = 8.6 Hz, 2 H), 7.40 (d, *J* = 8.2 Hz, 1 H), 7.35 (d, *J* = 8.0 Hz, 1 H), 7.31-7.28 (m, 4 H), 7.20-7.17 (m, 2 H), 7.07 (t, *J* = 7.4 Hz, 1 H), 6.97 (d, *J* = 8.9 Hz, 2 H), 6.65 (d, *J* = 8.9 Hz, 2 H), 6.53 (s, 1H), 3.83 (s, 3 H), 2.94 (s, 6 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 158.5, 149.9, 139.5, 137.5, 131.9, 131.6, 129.9, 129.2, 128.8, 126.1, 126.0, 122.9, 122.2, 121.9, 120.8, 120.6, 116.6, 114.6, 112.0, 111.9, 110.7, 55.5, 49.9, 40.2; ESI-MS calcd. for $C_{31}H_{27}BrN_3O$ (M+H): 536.1338; Found: 536.1342.

2-(4-(dimethylamino)phenyl)-2-(1-(4-methoxyphenyl)-1H-indol-3-yl)-2-(4-(trifluoromethyl)phenyl)acetonitrile (5d):

colorless solid, 197.7 mg, 84%; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.57 (m, 3 H), 7.42-7.29 (m, 3 H), 7.23-7.18 (m, 5 H), 7.07 (t, *J* = 8.0 Hz, 1 H), 6.97 (d, *J* = 8.8 Hz, 2 H), 6.65 (d, *J* = 8.9 Hz, 2 H), 6.53 (s, 1H), 3.83 (s, 3 H), 2.94 (s, 6 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 158.5, 150.4 (J_{C-F} = 7.5 Hz), 150.0, 144.4, 137.5, 131.9, 129.8, 129.5 (J_{C-F} = 31.4, 6.3 Hz), 129.2, 128.8, 128.5, 126.2, 125.9, 125.5, 123.0, 122.0, 120.8, 120.7, 120.1 (J_{C-F} = 4.6 Hz), 116.3, 114.7, 112.0, 110.7, 55.8, 50.3, 40.2; ESI-MS calcd. for $C_{32}H_{27}F_3N_3O$ (M+H): 526.2106; Found: 526.2116.

2-(4-(dimethylamino)phenyl)-2-(3-methoxyphenyl)-2-(1-(4-methoxyphenyl)-1H-indol-3-yl)acetonitrile (5e):

colorless solid, 155.1 mg, 71%; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.38 (d, *J* = 8.1 Hz, 2 H), 7.30 (d, *J* = 8.8 Hz, 2 H), 7.25-7.21 (m, 2 H), 7.18 (t, *J* = 8.1 Hz, 1 H), 7.05 (t, *J* = 7.8 Hz, 1 H), 7.00-6.96 (m, 5 H), 6.83 (dd, *J* = 7.7, 2.3 Hz, 1 H), 6.64 (d, *J* = 8.9 Hz, 2 H), 6.56 (s, 1H), 3.83 (s, 3 H), 3.73 (s, 3 H), 2.93 (s, 6 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 159.6, 158.4, 149.8, 141.9, 137.4, 132.1, 129.4, 129.2, 128.8, 126.8, 126.2, 126.1, 122.7, 122.6, 121.0, 120.6, 120.4, 117.1, 114.6, 114.3, 112.8, 112.0, 110.5, 55.5, 55.2, 50.3, 40.3; ESI-MS calcd. for $C_{32}H_{29}N_3NaO_2$ (M+Na): 510.2157; Found: 510.2134.

ethyl 2-(4-(dimethylamino)phenyl)-2-(1-(4-methoxyphenyl)-1H-indol-3-yl)-2-phenylacetate (5f):

colorless solid, 171.7 mg, 76%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40-7.32 (m, 4 H), 7.26-7.21 (m, 5 H), 7.10 (t, *J* = 8.1 Hz, 3 H), 6.97-6.19 (m, 3 H), 6.76 (s, 1 H), 6.62 (d, *J* = 8.9 Hz, 2 H), 4.27 (q, *J* = 14.1, 7.0 Hz, 2 H), 3.83 (s, 3 H), 3.73 (s, 3 H), 2.91 (s, 6 H), 1.18 (t, *J* = 7.0 Hz, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 174.0, 158.0, 149.1, 143.2, 137.1, 132.6, 131.1, 130.3, 129.6, 129.4, 128.3, 127.5, 126.5, 126.0, 122.9, 121.8, 120.1, 119.4, 114.5, 111.6, 110.1, 61.4, 55.5, 40.4, 14.0; ESI-MS calcd. for $C_{33}H_{32}N_2NaO_3$ (M+Na): 527.2311; Found: 527.2303.

1-(4-(dimethylamino)phenyl)-1-(1-(4-methoxyphenyl)-1H-indol-3-yl)-1-phenylpropan-2-one (5g):

colorless solid, 148.8 mg, 70%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42-7.35 (m, 4 H), 7.34-7.31 (m, 3 H), 7.26-7.22

(m, 3 H), 7.18-7.10 (m, 4 H), 7.03 (t, *J* = 6.6 Hz, 3 H), 7.00 (dd, *J* = 8.8, 2.0 Hz, 2 H), 6.93 (t, *J* = 7.8 Hz, 1 H), 6.63 (d, *J* = 8.9 Hz, 2 H), 3.85 (s, 3 H), 2.91 (s, 6 H), 2.16 (s, 3 H); ^{13}C NMR (175 MHz, $CDCl_3$): δ 207.1, 158.2, 149.0, 142.8, 137.0, 132.5, 130.4, 129.7, 129.6, 129.0, 128.1, 127.8, 127.7, 126.3, 126.0, 122.2, 122.2, 119.8, 118.2, 114.6, 111.8, 110.0, 66.9, 55.5, 40.3; ESI-MS calcd. for $C_{32}H_{31}N_2O_2$ (M+H): 475.2386; Found: 475.2373.

2-(1-(4-methoxyphenyl)-1H-indol-3-yl)-2-phenyl-2-(4-(phenylamino)phenyl)acetonitrile (6a):

colorless solid, 181.1 mg, 80%; ^{1}H NMR (700 MHz, $CDCl_3$): δ 7.44 (d, *J* = 7.3 Hz, 2 H), 7.41 (d, *J* = 8.3 Hz, 1 H), 7.38 (d, *J* = 8.0 Hz, 1 H), 7.35 (t, *J* = 7.0 Hz, 2 H),), 6.33-6.31 (m, 3 H),), 7.29-7.24 (m, 4 H), 7.21 (t, *J* = 7.3 Hz, 1 H), 7.09-7.06 (m, 3 H), 7.00 (d, *J* = 8.5 Hz, 2 H), 6.98 (d, *J* = 8.8 Hz, 2 H), 6.94 (t, *J* = 7.2 Hz, 1 H), 6.56 (s, 1 H), 5.77 (bs, 1 H), 3.84 (s, 3 H); ^{13}C NMR (175 MHz, $CDCl_3$): δ 158.5, 143.1, 142.1, 139.9, 137.5, 132.0, 131.3, 129.3, 129.2, 129.2, 128.6, 128.1, 127.9, 126.1, 122.9, 122.5, 121.6, 120.9, 120.5, 118.6, 116.8, 116.6, 114.7, 110.6, 55.5, 50.5; ESI-MS calcd. for $C_{35}H_{27}N_3NaO$ (M+Na): 528.2052; Found: 528.2046.

2-(1-(4-methoxyphenyl)-1H-indol-3-yl)-2-(4-(methyl(phenyl)amino)phenyl)-2-phenylacetonitrile (6b):

colorless solid, 217.8 mg, 85%; ^{1}H NMR (700 MHz, $CDCl_3$): δ 7.45 (d, *J* = 7.7 Hz, 2 H), 7.41-7.38 (m, 2 H), 7.35 (t, *J* = 7.1 Hz, 2 H),), 6.33-6.29 (m, 5 H),), 7.25-7.20 (m, 3 H), 7.12 (d, *J* = 7.6 Hz, 2 H), 7.08 (t, *J* = 7.2 Hz, 1 H), 7.06 (t, *J* = 6.8 Hz, 1 H), 6.99 (d, *J* = 8.8 Hz, 2 H), 6.87 (d, *J* = 8.8 Hz, 2 H), 6.59 (s, 1 H), 3.85 (s, 3 H), 3.31 (s, 3 H);; ^{13}C NMR (175 MHz, $CDCl_3$): δ 158.5, 148.5, 148.3, 140.0, 137.5, 132.0, 130.3, 129.3, 129.2, 128.9, 128.5, 128.1, 126.2, 125.8, 125.5, 123.2, 123.1, 122.8, 121.0, 120.5, 117.2, 116.9, 114.7, 114.7, 110.6, 55.5, 50.5, 40.1; ESI-MS calcd. for $C_{36}H_{29}N_3NaO$ (M+Na): 542.2208; Found: 542.2294.

2-(4-(butylamino)phenyl)-2-(1-(4-methoxyphenyl)-1H-indol-3-yl)-2-phenylacetonitrile (6c):

colorless semi-solid, 160.9 mg, 74%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43-7.36 (m, 4 H), 7.35-7.26 (m, 5 H), 7.19 (t, *J* = 8.1 Hz, 1 H), 7.15 (dd, *J* = 6.7, 1.8 Hz, 1 H), 7.05 (t, *J* = 7.1 Hz, 1 H), 6.96 (dd, *J* = 6.7, 2.0 Hz, 2 H), 6.54-6.52 (m, 3H), 3.83 (s, 3 H), 3.65 (bs, 1 H), 3.07 (t, *J* = 7.1 Hz, 2 H), 1.61-1.54 (m, 2 H), 1.45-1.35 (m, 2 H), 0.93 (t, *J* = 7.3 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.4, 148.1, 140.4, 137.5, 132.1, 129.3, 129.1, 128.5, 128.2, 127.8, 126.3, 126.1, 122.8, 122.1, 120.5, 117.3, 114.7, 112.3, 110.6, 55.6, 50.4, 43.5, 31.6, 20.2, 13.9; ESI-MS calcd. for $C_{33}H_{32}N_3O$ (M+H): 486.2545; Found: 486.2545.

2-(4-(butyl(methyl)amino)phenyl)-2-(1-(4-methoxyphenyl)-1H-indol-3-yl)-2-phenylacetonitrile (6d):

colorless semi-solid, 183.5 mg, 82%; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.43-7.42 (m, 2 H), 7.40-7.36 (m, 2 H), 7.34-7.27 (m, 6 H), 7.18 (d, *J* = 8.8 Hz, 2 H), 7.05 (t, *J* = 7.2 Hz, 1 H), 6.96 (d, *J* = 8.8 Hz, 2 H), 6.66 (d, *J* = 8.8 Hz, 2 H), 6.56 (s, 1H), 3.38 (s, 3 H), 3.26 (t, *J* = 7.6 Hz, 2 H), 2.90 (s, 3 H), 1.54-1.50 (m, 2 H), 1.34-1.28 (m, 2 H), 0.91 (t, *J* = 7.3 Hz, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 158.4, 148.7, 140.4, 137.4, 132.1, 129.6, 129.2, 128.9, 128.4, 128.1, 127.7, 126.1, 125.8, 125.4, 122.7, 121.0, 120.4, 117.3, 114.7, 114.6, 111.5, 110.5, 55.5, 52.4, 50.3, 38.1, 28.8, 13.9; ESI-MS calcd. for $C_{34}H_{34}N_3O$ (M+H): 500.2702; Found: 500.2701.

2-(4-((2-methoxyethyl)amino)phenyl)-2-(1-(4-methoxyphenyl)-1H-indol-3-yl)-2-phenylacetonitrile (6e):

Yellow semi-solid, 152.8 mg, 70%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42-7.37 (m, 3 H), 7.35-7.27 (m, 6 H), 7.21-7.15 (m, 3 H), 7.05 (t, *J* = 8.8 Hz, 1 H), 6.97 (dd, *J* = 6.7, 2.2 Hz, 2 H), 6.57 (d, *J* = 8.7 Hz, 2 H), 6.53 (s, 1H), 3.83 (s, 3 H), 3.59 (bs, 1 H), 3.58 (t, *J* = 5.3 Hz, 2 H), 3.56 (s, 3 H), 3.25 (t, *J* = 5.0 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.4, 147.8 140.3, 137.5, 132.1, 129.8, 129.3, 129.1, 128.9, 128.5, 128.3, 128.1, 127.8, 126.1, 122.8, 121.0, 120.5, 117.2, 114.7, 112.8, 110.6, 58.7, 55.6, 43.3; ESI-MS calcd. for $C_{32}H_{30}N_3O_2$ (M+H): 488.2338; Found: 488.2337.

2-(4-((2-methoxyethyl)(methyl)amino)phenyl)-2-(1-(4-methoxyphenyl)-1H-indol-3-yl)-2-phenylacetonitrile (6f):

colorless solid, 193.2 mg, 86%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43-7.38 (m, 3 H), 7.36-7.29 (m, 6 H), 7.20-7.17 (m, 3 H), 7.06 (t, *J* = 7.9 Hz, 1 H), 6.97 (d, *J* = 8.9 Hz, 2 H), 6.65 (d, *J* = 8.9 Hz, 2 H), 6.55 (s, 1H), 3.83 (s, 3 H), 3.54-3.47 (m, 4 H), 3.33 (s, 3 H), 2.97 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.4, 148.7, 140.4, 137.5, 132.1, 129.3, 129.0, 128.5, 128.1, 127.8, 126.8, 126.3, 126.2, 122.8, 121.1, 120.5, 117.2, 114.7, 111.7, 110.6, 70.1, 59.0, 55.6, 52.3, 50.3, 38.8; ESI-MS calcd. for $C_{33}H_{31}N_3NaO_2$ (M+Na): 524.2314; Found: 524.2311.

2-(4-(bis(2-methoxyethyl)amino)phenyl)-2-(1-(4-methoxyphenyl)-1H-indol-3-yl)-2-phenylacetonitrile (6g):

colorless solid, 200.4 mg, 82%; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.44-7.37 (m, 4 H), 7.35-7.28 (m, 5 H), 7.21-7.17 (m, 3 H), 7.06 (td, *J* = 8.2, 0.9 Hz, 1 H), 6.97 (dd, *J* = 6.7, 2.2 Hz, 2 H), 6.64 (d, *J* = 9.0 Hz, 2 H), 6.57 (s, 1H), 3.83 (s, 3 H), 3.54-3.52 (m, 8 H), 3.33 (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 158.4, 147.7, 140.3, 137.5, 132.1, 129.3, 129.1, 128.5, 128.1, 127.7, 126.7, 126.2, 122.8, 121.0, 120.4, 117.2, 116.1, 114.7, 111.7, 111.4, 110.6, 70.1, 70.0, 58.9, 55.5, 50.9, 50.8, 50.3; ESI-MS calcd. for $C_{35}H_{35}N_3NaO_3$ (M+Na): 568.2576; Found: 568.2584.

2-(1-(4-methoxyphenyl)-1H-indol-3-yl)-2-(4-morpholinophenyl)-2-phenylacetonitrile (6h):

yellow semi-solid, 143.2 mg, 64%; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.41-7.39 (m, 2 H), 7.36-7.23 (m, 3 H), 7.32-7.27 (m, 6 H), 7.19 (t, *J* = 7.2 Hz, 1 H), 7.06 (t, *J* = 7.1 Hz, 1 H), 6.97 (d, *J* = 8.9 Hz, 2 H), 6.85 (d, *J* = 8.5 Hz, 2 H), 6.52 (s, 1H), 3.84-3.82 (m, 7 H), 3.15 (t, *J* = 4.4 Hz, 4 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 158.4, 139.9, 137.4, 131.9, 130.5, 129.2, 129.0, 128.5, 128.1, 127.9, 126.1, 122.8, 122.4, 120.9, 12.5, 116.8, 115.0, 114.6, 110.6, 67.7, 55.5, 50.4, 48.7; ESI-MS calcd. for $C_{33}H_{30}N_3O_2$ (M+H): 500.2338; Found: 500.2345.

2-(4-((4-methoxybenzyl)amino)phenyl)-2-(1-(4-methoxyphenyl)-1H-indol-3-yl)-2-phenylacetonitrile (4m):

colorless solid, 160.0 mg, 65%; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.42-7.40 (m, 2 H), 7.38-7.35 (m, 2 H), 7.33-7.29 (m, 5 H), 7.25 (d, *J* = 8.5 Hz, 2 H), 7.20-7.15 (m, 3 H), 7.06 (d, *J* = 7.8 Hz, 1 H), 6.97 (d, *J* = 8.8 Hz, 2 H), 6.86 (d, *J* = 8.5 Hz, 2 H), 6.57 (d, *J* = 8.7 Hz, 2 H), 6.54 (s, 1H), 4.21 (s, 2 H), 4.03 (bs, 1 H) 3.83 (s, 3 H), 3.78 (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 158.9, 158.4, 147.7, 140.2, 137.5, 132.0, 130.9, 129.2, 129.1, 128.8, 128.5, 128.2, 128.1, 127.8, 126.2, 126.1, 122.8, 122.7, 121.0, 120.4, 117.1, 114.6, 114.0, 112.5, 110.6, 55.5, 55.2, 50.4, 47.7; ESI-MS calcd. for $C_{37}H_{31}N_3NaO_2$ (M+Na): 572.2314; Found: 572.2394.

2-(4-aminophenyl)-2-(1-(4-methoxyphenyl)-1H-indol-3-yl)-2-phenylacetonitrile (4n):

colorless solid, 68.7 mg, 88%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42-7.39 (m, 3 H), 7.37-7.33 (m, 2 H), 7.31-7.29 (m, 4 H), 7.19 (t, *J* = 7.2 Hz, 1 H), 7.15 (dd, *J* = 6.6, 1.9 Hz, 2 H),

7.06 (t, *J* = 7.1 Hz, 1 H), 6.96 (dd, *J* = 6.8, 2.0 Hz, 2 H), 6.62 (dd, *J* = 6.6, 1.9 Hz, 2 H), 6.53 (s, 1H), 3.71 (bs, 2 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 158.4, 146.0, 140.1, 137.5, 132.0, 129.4, 129.3, 129.2, 128.5, 128.1, 127.8, 126.2, 126.1, 122.8, 122.6, 121.0, 120.5, 117.0, 114.9, .114.6, 110.6, 55.5, 50.4; ESI-MS calcd. for $C_{29}H_{23}N_3NaO$ (M+Na): 452.1739; Found: 452.1747.

2-(4-iodophenyl)-2-(1-(4-methoxyphenyl)-1H-indol-3-yl)-2-phenylacetonitrile (4o):

colorless solid, 115.7 mg, 92%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (dd, *J* = 6.6, 1.9 Hz, 2 H), 7.41-3.36 (m, 3 H), 7.36-7.32 (m, 3 H), 7.29 (d, *J* = 8.8 Hz, 2 H), 7.24-7.19 (m, 1 H), 7.15 (dd, *J* = 6.6, 1.9 Hz, 2 H), 7.08 (td, *J* = 7.1, 0.9 Hz, 1 H), 6.97 (dd, *J* = 6.7, 2.3 Hz, 2 H), 6.49 (s, 1H), 3.83 (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 158.6, 139.5, 139.0, 137.8, 137.6, 131.8, 130.1, 129.3, 128.8, 128.6, 128.3, 128.0, 126.2. 125.9, 123.1, 121.8, 120.7, 115.8, 114.7, 110.8, 94.1, 55.6, 50.9; ESI-MS calcd. for $C_{29}H_{21}IN_2NaO$ (M+Na): 563.0596; Found: 563.0596.

2-(4-bromophenyl)-2-(1-(4-methoxyphenyl)-1H-indol-3-yl)-2-phenylacetonitrile (4q):

colorless semi-solid, 91.8 mg, 80%; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.67 (d, *J* = 8.6 Hz, 2 H), 7.42-7.38 (m, 3 H), 7.36-7.32 (m, 4 H), 7.31-7.29 (m, 2 H), 7.20 (t, *J* = 7.3 Hz, 1 H), 7.16 (d, *J* = 8.6 Hz, 2 H), 7.08 (t, *J* = 8.0 Hz, 1 H), 6.97 (m, 2 H), 6.51 (s, 1H), 3.84 (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 158.6, 139.6, 139.0, 137.8, 137.6, 130.1, 129.3, 128.8, 128.6, 128.3, 128.2, 128.0, 126.2, 125.9, 123.1, 121.8, 120.9, 120.7, 114.7, 110.8, 94.0, 55.5, 50.9; EI-MS calcd. for $C_{29}H_{21}BrN_2O$ (M+): 492.0837; Found: 492.0842.

2-(1-(4-methoxyphenyl)-1H-indol-3-yl)-2,2-diphenylacetonitrile (4p):

colorless liquid, 55.0 mg, 57%; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.42-7.39 (m, 5 H), 7.36-7.31 (m, 7 H), 7.29 (dd, *J* = 6.6, 2.1 Hz, 2 H), 7.20 (t, *J* = 8.1 Hz, 1 H), 7.06 (td, *J* = 8.0, 0.7 Hz, 1 H), 6.97 (dd, *J* = 6.7, 2.1 Hz, 2 H), 6.50 (s, 1H), 3.83 (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 158.5, 139.6, 137.5, 131.9, 129.3, 128.6, 128.2, 128.0, 126.2, 122.9, 122.3, 120.9, 120.6, 116.5, 114.7, 110.7, 55.5, 51.2; ESI-MS calcd. for $C_{29}H_{22}N_2NaO$ (M+Na): 437.1630; Found: 437.1625.

2-(4-(bis(2-methoxyethyl)amino)phenyl)-2-(4-(dimethylamino)phenyl)-2-phenylacetonitrile (7b):

colorless liquid, 230.6 mg, 63%; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.31-7.23 (m, 5 H), 7.03 (dd, *J* = 6.8, 2.2 Hz, 2 H), 6.98 (dd, *J* = 6.8, 2.1 Hz, 2 H), 6.63 (dd, *J* = 6.8, 2.2 Hz, 2 H), 6.61 (dd, *J* = 6.8, 2.1 Hz, 2 H), 3.53-3.50 (m, 8 H), 3.33 (s, 6 H), 2.93 (s, 6 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 149.7, 147.2, 141.6, 129.7, 129.4, 128.6, 128.3, 128.2, 127.9, 127.5, 124.2, 111.9, 111.3, 70.0, 58.9, 55.8. 50.8, 40.3; ESI-MS calcd. for $C_{28}H_{34}N_3O_2$ (M+H): 444.2651, found: 444.2655.

Acknowledgements

We thank the Ministry of Education (MOE 106N506CE1) and the Ministry of Science and Technology (MOST 107- 3017-F-007-002), Taiwan, for financial support of this work.

References

[1] a) M. P. Doyle, In *Comprehensive Organometallic Chemistry II*, Abel, E. W.; Stone, F. G. A., Ed.; Pergamon: Oxford UK, *12*, 387-469; b) M. P. Doyle, McKervy, M. A.; Ye, T. *Modern Catalytic Method for Organic Synthesis with Diazo compounds*: *From Cyclopropanes to Ylides*; Wiley; New York USA, **1998**; c) H. M. L. Davies, R. E. J. Beckwith, *Chem. Rev.*, **2003**, *103*, 2861-2904; d) L. Liu, J. Zhang, *Chem. Soc. Rev.*, **2016**, *45*, 506-516; e) M. R. Fructos, M. M. Díaz-Requejo, P. J. Pérez, *Chem. Commun.* **2016**, *52*, 7326-7335.

[2] For gold carbenes derived from diazo precursors, see selected papers: a) M. R. Fructos, T. R. Belderrain, P. de Fremont, N. M. Scott, S. P. Nolan, M. M. Requejo, P. J. Perez, *Angew. Chem., Int. Ed*., **2005**, ***44***, 5284-5288; b) G. Xu, C. Zhu, W. Gu, J. Li, J. Sun, *Angew. Chem., Int. Ed*., **2015**, *54*, 883-887; c) J. Barluenga, G. Lonzi, M. Tomas, L. A. Lopez, *Chem. Eur. J*., **2013**, *19*, 1573-1576; d) J. F. Briones, H. M. L. Davies, *J. Am. Chem. Soc*., **2012**, *134*, 1191611919; e) V. V. Pagar, A. M. Jadhav, R.-S. Liu, *J. Am. Chem. Soc*., **2011**, *133*, 20728-20731; f) A. M. Jadhav, V. V. Pagar, R.-S. Liu, *Angew. Chem., Int. Ed*., **2012**, *51*, 11809-11813; g) V. V. Pagar, R.-S. Liu, *Angew. Chem., Int. Ed*., **2015**, *54*, 4923-4926. h) L. N. S. Comprido, J. E. M. N. Klein, G. Knizia, J. Kastner, A. S. K. Hashmi, *Angew. Chem. Int. Ed*., **2015**, *54*,10336 –10340. i) L. N. S. Comprido, J. E. M. N. Klein, G. Knizia, J. Kastner, A. S. K. Hashmi, *Chem. Eur. J*., **2016**, *22*, 2892 –2895.

[3] For Au see: a) Z. Yu, B. Ma, M. Chen, H.-H. Wu, L. Liu, J. Zhang, *J. Am. Chem. Soc*., **2014**, *136*, 6904-6907; b) Y. Xi, Y. Su, Z. Yu, B. Dong, E. J. McClain, Y. Lan, X. Shi, *Angew. Chem., Int. Ed.*, **2014**, *53***,** 9817-9821; c) E. López, G. Lonzi, L. A. López, *Organometallics*, **2014**, *33*, 5924-5927; d) I. Rivilla, B. P. Gõmez-Emeterio, M. R. Fructos, M. M. Díaz-Requejo, P. J. Pérez, *Organometallics*, **2011**, *30*, 2855-2860.

[4] For Rh, Cu, Ag, Pd: see: a) M. P. Doyle, R. Duffy, M. Ratnikov, L. Zhou, *Chem. Rev.*, **2010**, *110*, 704-724; b) H. M. L. Davies, Y.-J. Lian, *Acc. Chem. Res.* **2012**, 45, 923-935; c) H. M. L. Davies, D. Mo-rton, *Chem. Soc. Rev.* **2011**, *40*, 1857-1869; d) M. M. Díaz-Requejo, P. J. Pérez, *Chem. Rev.* **2008**, *108*, 3379-3394; e) Z. Liu, J. Wang, *J. Org. Chem.* **2013**, *78*, 10024-10030; f) A. DeAngelis, V. W. Shurtleff, O. Dmitrenko, J. M. Fox, *J. Am. Chem.Soc.* **2011**, *133*, 1650-1653; g) M. J. Rosenfeld, B. K. Shankar, H. Shechter, *J. Org. Chem.* **1988**, *53*, 2699-2705; h) D. Yadagiri, P. Anbarasan, *Org. Lett.* **2014**, *16*, 2510-2513; i) W.-W. Chan, S.-F. Lo, Z. Zhou, W.-Y. Yu, *J. Am. Chem. Soc.* **2012**, *134*, 13565-13568; j) T. K. Hyster, K. E. Ruhl, T. Rovis, *J. Am. Chem Soc.*, **2013**, *135*, 5364-5367.

[5] For Cu: see: a) T. C. Maier, G. C. Fu, *J. Am. Chem. Soc.* **2006**, *128*, 4594-4595; b) C. Chen, S.-F. Zhu, B. Liu, L.-X. Wang, Q.-L. Zhou, *J. Am. Chem. Soc.* **2007**, *129*, 12616-12617; For Pd see: c) X.-L. Xie, S.-F. Zhu, J.-X. Guo, Y. Cai, Q.-L. Zhou, *Angew. Chem. Int. Ed.*, **2014**, *53*, 2978-2981.

[6] a) X. Guo, W.-H. Hu, *Acc. Chem. Res.*, **2013**, *46*, 2427-2440; b) H. Qiu, M. Li, L.-Q. Jiang, F.-P. Lv, L. Zan, C.-W. Zhai, M. P. Doyle, W.-H. Hu, *Nat. Chem.*, **2012**, *4*, 733-738; c) X. Guan, L. Yang, W.-H. Hu, *Angew. Chem.*,

Int. Ed., **2010**, *49*, 2190-2192; d) C.-C. Jing, D. Xing, W.-H. Hu, *Org. Lett.*, **2015**, *17*, 4336-4339; e) J. Jiang, X.-C. Ma, S.-Y. Liu, Y. Qian, F.-P. Li, L. Qiu, X. Wu, W.-H. Hu, *Chem. Commun.*, **2013**, *49*, 4238-4240.

[7] R. R. Singh, R.-S. Liu, *Chem. Commun.*, **2017**, *53*, 4593-4596.

[8] Metal carbenes as dication synthons was previous reported in a stoichiometric fashion whereas this system is preformed catalytically. See K.-W. Liang, W.-T. Li, G.-H. Lee, S.-M. Peng, R.-S. Liu, *J. Am. Chem. Soc*., **1997**, *119*, 4404-4412.

[9] See selected Reviews: a) C. S. Yeung, V. M. Dong, *Chem. Rev.*, **2011**, *111*, 1215-1292; b) C. Liu, H. Zhang, W. Shi, A. Lei, *Chem. Rev.*, **2011**, *111*, 1780-1824; c) I. Hussain, T. Singh, Adv. *Synth. Catal.*, **2014**, *356*, 1661-1696; d) N. Kuhl, M. N. Hopkinson, J. Wencel-Delord, F. Glorius, *Angew. Chem. Int. Ed.*, **2012**, *51*, 10236-10254; e) J. A. Ashenhurst, *Chem. Soc. Rev.*, **2010**, *39*, 540-548.

[10] a) P. Christ, A. G. Lindsay, S. S. Vormittag, J.-M. Neudçrfl, A. Berkessel, M-A. C. O'Donoghue, *Chem. Eur. J*. **2011**, *17*, 8524–8528. b) R. Kather, E. Rychagova, P.-S. Camacho, S. E. Ashbrook, J. D. Woollins, L. Robben, E. Lork, S. Ketkov, J. Beckmann, *Chem. Commun*., **2016**, *52*, 10992-10995.

[11] CCDC-2009271 contains the supplementary crystallographic data for this paper (**4b)**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[12] T. J. Heckrodt, Y. Chen, R. Singh, *Tetrahedron.*, **2019**, *75*, 2385-2399.

[13] a) S. Maity, D. Das, S. Sarkar, R. Samanta, *Org. Lett.* **2018**, *20*, 5167–5171. b) Q. Wang, J. Yang, Y. Zheng, X. Liao, *J. Chem. Res.*, **2017**, *41*, 193–194.

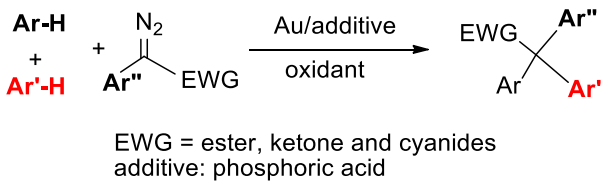
10.1002/adsc.202000879

FULL PAPER

Gold-catalyzed Oxidative Cross-coupling Reactions Among Two Distinct Arenes and One Gold Carbene with Phosphoric Acids as Cocatalysts

Adv. Synth. Catal. **Year**, *Volume*, Page – Page

M. D. Patil, B. S. Kale and R.-S. Liu*



EWG = ester, ketone and cyanides
additive: phosphoric acid