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Au^I-Catalyzed Direct Hydroamination/Hydroarylation and Double Hydroamination of Terminal Alkynes

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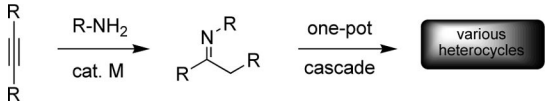
An efficient method for formal Markownikoff hydroamination/hydroarylation and double hydroamination of terminal alkynes has been developed. For example, treatment of terminal alkynes with amino-aromatics or diamines in the presence of 2–5 mol-% of $Ph_3PAuNTf_2$ in toluene at 100 °C gave the corresponding products in excellent yields. The method was shown to be applicable to a broad range of substrates and, more importantly, unlike our previously reported method, a tethered hydroxy group in the alkyne is not necessary. The mechanism of the reaction is also discussed.

Introduction

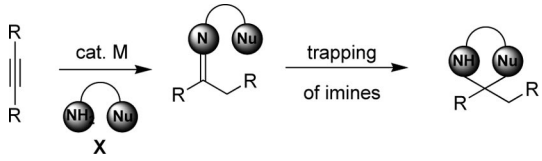
The addition of an N–H bond across an unactivated C–C triple bond is one of the simplest and atom-economical[1] synthetic transformations for the formation of C–N bonds. Catalysts derived from both early and late transition metals[2] as well as lanthanides[3] have shown significant activity for the addition of N–H bonds across alkynes. These processes[4] are potentially useful since imines/enamines that are generated in situ can be converted into various heterocycles[5] by cascade[6] design in one pot [Equation (1)].



(1)

Synthetic methods relying on π-acid catalysts have recently been the focus of intense development.[7] In these transformations, through the interaction of the alkyne with a π-acidic metal, the electron density of the triple bond is reduced, thereby rendering it electrophilic. A tethered nucleophile may undergo addition followed by subsequent transformations to produce heterocycles. Out of the various types of reactions catalyzed by π-acids, double addition of nucleophiles to triple bonds is very important from a synthetic point of view. In this regard, reactions such as hydroalkoxylation/hydroarylation,[8] double hydroalkoxylation,[9] double hydroarylation,[10] and hydroamination/hydrophosphanation[11] of alkynes have been reported in the literature. However, there are very few reports on hydroamination/hydroarylation and double hydroamination of alkynes. Yi and Yun reported the use of a cationic ruthenium hydride complex as a catalyst for the formal hydroamination/hydroarylation of terminal alkynes that proceeds with C–H activation.[12] Dixon and co-workers reported a gold-catalyzed cyclization of alkynoic acids with amino-aromatics involving a formal hydroamination/hydroarylation.[13] Recently, a Cu^I-catalyzed tandem hydroamination/alkynylation of alkynes has been reported by Xu and Hammond.[14]

We assumed that the amine **X** would attack an electrophilically activated alkyne to generate an imine, which then becomes a new electrophilic precursor capable of reacting with a second tethered nucleophile (Nu = Ar or NH_2) to give a double addition product [Equation (2)]. A reaction as envisioned could be considered as a hydroamination/hydroarylation (when Nu = Ar) and double hydroamination (when Nu = NH_2), which would provide access to a wide variety of nitrogen-containing heterocycles.



(2)

Previously, we reported double hydroamination[15] and hydroamination/hydroarylation[16] cascade reactions of terminal alkynes bearing a hydroxy group in the proximity (Figure 1, path a). A proximal hydroxy group proved to be necessary for the reaction to occur; alkynes with no hydroxy group in the tether (e.g., 1-octyne) failed to react. In this paper, we report the $Ph_3PAuNTf_2$-catalyzed direct hydroamination/hydroarylation and double hydroamination of terminal alkynes having no proximal hydroxy group (Figure 1, path b). The transformation shows a very broad sub-

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strate scope towards diversely substituted amino-aromatics or diamines and terminal alkynes and, thus, provides efficient access to multi-substituted nitrogen-containing heterocycles, such as pyrrolo[1,2-*a*]quinoxalines,[17] indolo[3,2-*c*]quinolines,[18] indolo[1,2-*a*]quinoxalines,[19] tetrahydro-4-quinazolinones,[20] and benzo[4,5]imidazo[1,2-*c*]quinazolines;[21] members of this class of compounds are known to exhibit interesting biological activities.

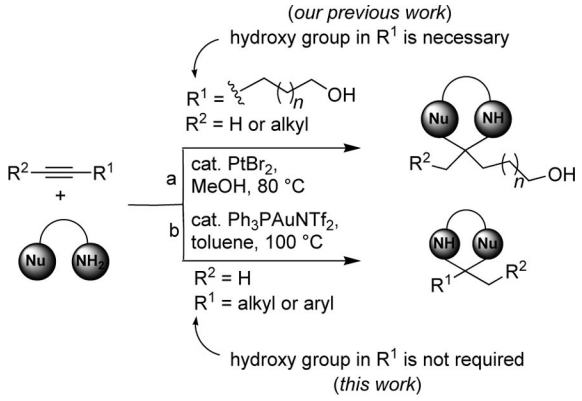
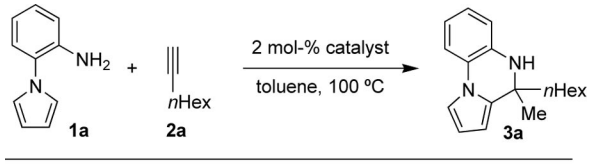


Figure 1. Concept of intermolecular hydroamination/hydroarylation and double hydroamination of terminal alkynes.

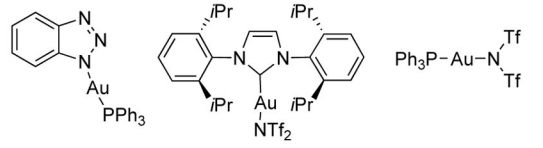
Results and Discussion

Initial efforts were directed towards finding an appropriate metal catalyst for the proposed reaction of 2-aminophenylpyrrole (**1a**) with 1-octyne (**2a**) as model substrates. Preliminary optimization studies revealed that the use of a nonpolar, noncoordinating solvent such as toluene was found to be the best.[22] Therefore, with toluene as solvent, a series of π-acidic catalysts were screened, and the results are outlined in Table 1. Based on our earlier report,[15,16] the reaction was initially conducted by using platinum catalysts, such as $PtCl_2$, $PtBr_2$ or $PtCl_4$; however, lower yields were obtained in all cases (Entries 1–3). The catalysts AgOTf and $Cu(OTf)_2$ gave **3a** in 20 and 40% yields, respectively (Entries 4 and 5). Next, we turned our attention towards gold catalysts. A marginal increase in yield (50%) was observed when AuCl was employed (Entry 6). A combination of Ph_3PAuCl with various silver salts, such as AgOTf (Entry 7), $AgSbF_6$ (Entry 8), and $AgBF_4$ (Entry 9) was examined; of these, the former catalytic system proved to be the best, giving **3a** in 75% yield (Entry 7). No significant improvement in yield was observed when the reaction mixture was heated for 48 h (compare Entries 10 and 7); in this case, **1a** was recovered in 20% yield. This observation can be explained on the basis of the instability of $Ph_3PAuOTf$ at high temperature. Therefore, we planned to test the activity of thermally stable cationic Au^I catalysts for the present transformation. To this end, thermally stable Au^I complexes, such as $Ph_3PAuBtz$ (**I**),[23] $IPrAuNTf_2$ (**II**),[24] and $Ph_3PAuNTf_2$ (**III**) (Gagosz catalyst),[25] were prepared, and their catalytic activities were examined. Unfortunately, the catalyst $Ph_3PAuBtz$ (**I**) did not work at all; only starting material **1a** was recovered (Entry 11). On the other hand, catalyst $IPrAuNTf_2$ (**II**) produced **3a** in 81% yield (Entry 12). Pleasingly, the Gagosz catalyst (**III**) worked exceedingly well, to give **3a** in 90% yield (Entry 13). When the catalyst loading was lowered (1 mol-%), a marginal decrease in yield was observed (Entry 14).

Table 1. Optimization studies for the reaction between **1a** and **2a**.[a]



Entry	Catalyst	Time (h)	Yield[b]
1	$PtCl_2$	24	30%[c]
2	$PtBr_2$	24	20%[c]
3	$PtCl_4$	24	25%[c]
4	AgOTf	24	20%[c]
5	$Cu(OTf)_2$	24	40%[c]
6	AuCl	24	50%[d]
7	$Ph_3PAuCl/AgOTf$	24	75%[d]
8	$Ph_3PAuCl/AgSbF_6$	24	71%[d]
9	$Ph_3PAuCl/AgBF_4$	24	68%[d]
10	$Ph_3PAuCl/AgOTf$	48	77%[d]
11	$Ph_3PAuBtz$ (**I**)	24	00%[e]
12	$IPrAuNTf_2$ (**II**)	24	81%
13	***$Ph_3PAuNTf_2$ (III)***	***24***	***90%***
14	$Ph_3PAuNTf_2$ (**III**)	24	81%[f]
15	Tf_2NH	48	00%[e]



$Ph_3PAuBtz$ (**I**) $IPrAuNTf_2$ (**II**) Gagosz catalyst (**III**)

[a] Reaction conditions: **1a** (0.316 mmol), **2a** (0.379 mmol), catalyst (2 mol-%), toluene (2 mL), 100 °C. [b] Yield of isolated and chromatographically purified material. [c] 60–70% recovery of **1a**. [d] 20–40% recovery of **1a**. [e] Quantitative recovery of **1a**. [f] 1 mol-% of catalyst was used.

During the course of the reaction, traces of Tf_2NH could be generated from $Ph_3PAuNTf_2$ either in the presence of **1a** or trace amount of water present in the reaction medium. A Brønsted acid thus formed might act as catalyst for the present transformation.[26] To test this, the reaction was conducted with **1a** and **2a** in the presence of 2 mol-% Tf_2NH (Entry 15); under these conditions, **1a** was recovered rather than the product **3a**, which was not obtained. This clearly indicates that the $Ph_3PAuNTf_2$ catalyst is responsible for the reaction.

Inspired by the high degree of catalytic activity exhibited by the Gagosz catalyst, the scope of this transformation was then explored under optimized conditions (Table 1, Entry 13).

The results are summarized in Table 2. From Entries 1–6, it can be seen that a wide range of *N*-(2-aminophenyl)-pyrrole derivatives (bearing Me, OMe, COOMe, or Cl) **1b**–

g reacted well with 1-octyne (**2a**) to give products **3b**–**g** in moderate to high yields (65–89%). However, the reaction of fluoro derivative **1h** proved to be sluggish; the fluoro-substituted pyrrolo[1,2-*a*]quinoxalines **3h** was isolated in only 48% yield, even after heating for 48 h (Entry 7). Next, by keeping *N*-(2-aminophenyl)pyrrole (**1a**) as a substrate, a number of terminal alkynes were submitted to the reaction conditions (Entries 8–16). For example, 4-phenyl-1-butyne (**2b**) and propargyl alcohol (**2c**) reacted well with **1a**, and the desired products **3i** and **3j** were obtained in 75 and 67% yields, respectively. Interestingly, the present catalytic system was not appropriate for the reaction between *N*-(2-aminophenyl)pyrrole and aromatic alkynes, such as phenylacetylene (**2d**).[27] The use of AgOTf as catalyst was found to be necessary to obtain the product in higher yields (Entry 10). As exemplified in Entries 11 and 12, this method is not applicable to aromatic alkynes having either strong electron-donating or -withdrawing groups. In the case of

Table 2. $Ph_3PAuNTf_2$-catalyzed hydroamination/hydroarylation of terminal alkynes.[a]

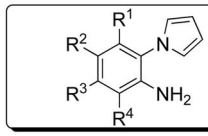
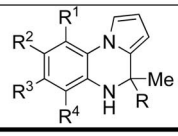
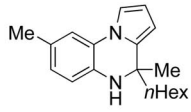
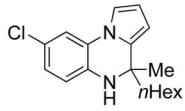
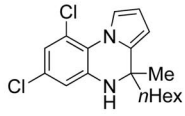
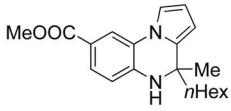
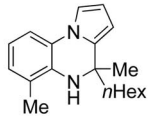
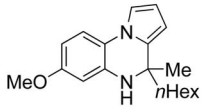
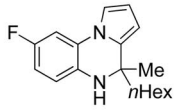
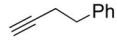
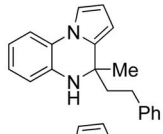
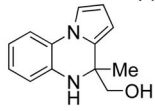
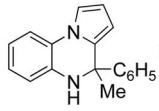
Entry	1	2	3	Yield[b]
				
1	**1b** $R^1 = R^3 = R^4 = H$, $R^2 = Me$	**2a**		**3b** 87%
2	**1c** $R^1 = R^3 = R^4 = H$, $R^2 = Cl$	**2a**		**3c** 83%
3	**1d** $R^2 = R^4 = H$, $R^1 = R^3 = Cl$	**2a**		**3d** 75%
4	**1e** $R^1 = R^3 = R^4 = H$, $R^2 = COOMe$	**2a**		**3e** 72%
5	**1f** $R^1 = R^2 = R^3 = H$, $R^4 = Me$	**2a**		**3f** 65%
6	**1g** $R^1 = R^2 = R^4 = H$, $R^3 = OMe$	**2a**		**3g** 89%
7	**1h** $R^1 = R^3 = R^4 = H$, $R^2 = F$	**2a**		**3h** 48%[c]
8	**1a**	 **2b**		**3i** 75%
9	**1a**	 **2c**		**3j** 67%
10	**1a**	 **2d**		**3k** 97%[d]

Table 2. *(Continued)*

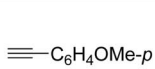
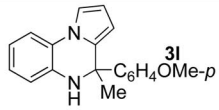
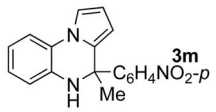
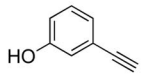
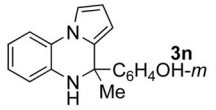
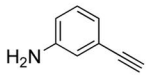
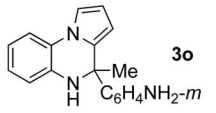
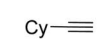
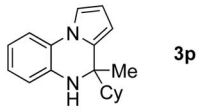
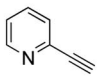
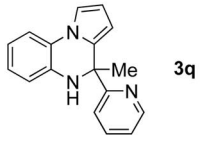
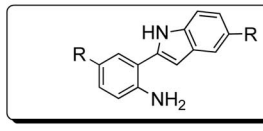
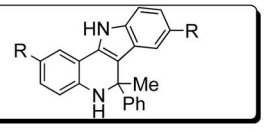
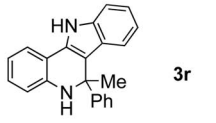
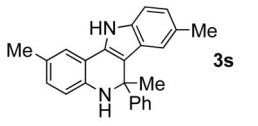
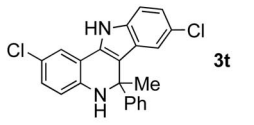
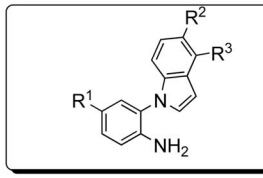
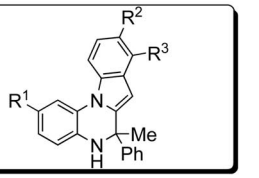
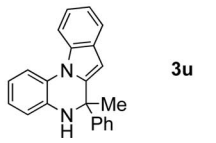
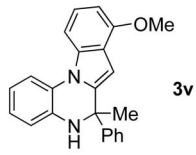
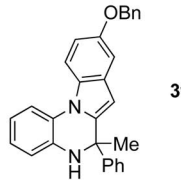
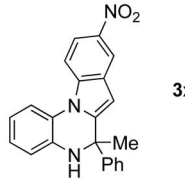
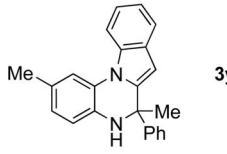
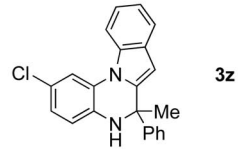
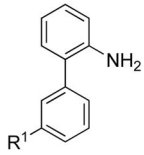
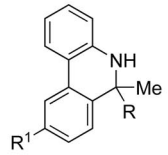
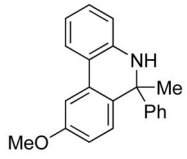
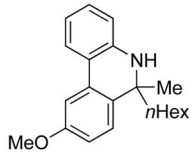
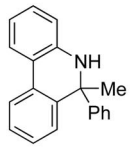
Entry	1		2	3	Yield[b]
11	**1a**		**2e**	 **3l**	50%[d]
12	**1a**		**2f**	 **3m**	00%[e]
13	**1a**		**2g**	 **3n**	78%
14	**1a**		**2h**	 **3o**	67%
15	**1a**		**2i**	 **3p**	94%
16	**1a**		**2j**	 **3q**	53%
					
17	**1i** R = H		**2d**	 **3r**	90%
18	**1j** R = Me		**2d**	 **3s**	92%
19	**1k** R = Cl		**2d**	 **3t**	95%
					
20	**1l** $R^1 = R^2 = R^3 = H$		**2d**	 **3u**	96%

Table 2. *(Continued)*

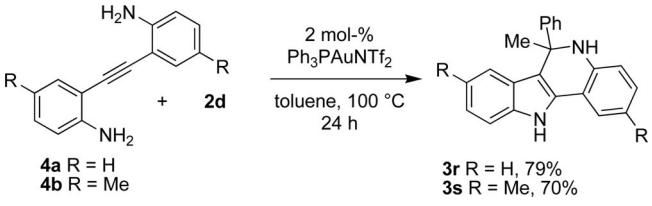
Entry	1	2	3		Yield[b]
21	**1m** $R^1 = R^2 = H$, $R^3 = OMe$	**2d**		**3v**	98%
22	**1n** $R^1 = R^3 = H$, $R^2 = OBn$	**2d**		**3w**	75%
23	**1o** $R^1 = R^3 = H$, $R^2 = NO_2$	**2d**		**3x**	72%[f]
24	**1p** $R^2 = R^3 = H$, $R^1 = Me$	**2d**		**3y**	75%
25	**1q** $R^2 = R^3 = H$, $R^1 = Cl$	**2d**		**3z**	70%
					
26	**1r** $R^1 = OMe$	**2d**		**3aa**	75%[g]
27	**1r** $R^1 = OMe$	**2a**		**3ab**	72%[g]
28	**1s** $R^1 = H$	**2d**		**3ac**	30%[h]

[a] Reaction conditions: **1** (0.316 mmol), **2** (0.379 mmol), $Ph_3PAuNTf_2$ (2 mol-%), toluene (2 mL), 100 °C, 24 h. [b] Yield of isolated and chromatographically purified material. [c] Reaction mixture was heated for 48 h. [d] AgOTf (10 mol-%) was used as catalyst. [e] **1a** was recovered when AgOTf (10 mol-%) and $Ph_3PAuNTf_2$ (2 mol-%) were used independently. [f] A combination of Ph_3PAuCl and AgOTf (5 mol-% each) was used. [g] **1r** was recovered in nearly 15–20% yield. [h] **1s** was recovered in ca. 60% yield.

(*p*-methoxyphenyl)acetylene (**2e**), only 50% yield of **3l** was obtained when AgOTf was used as catalyst (Entry 11); on the other hand, (*p*-nitrophenyl)acetylene was found to be inert under silver and gold catalysis (Entry 12). Free hydroxy or amino groups on the aromatic alkynes were tolerated well under the present reaction conditions. Thus, when **2g** or **2h** were treated with **1a**, the corresponding products **3n** and **3o** were obtained in 78 and 67% yields, respectively (Entries 13 and 14). Sterically hindered cyclohexylacetylene (**2i**) gave **3p** in 94% yield (Entry 15).

It is of interest to note that the catalyst system tolerates the pyridine ring. The reaction between **1a** and **2j** under the standard reaction conditions afforded pyridine-containing compound **3q**, albeit in 53% yield (Entry 16). When 2-(2-aminophenyl)indoles **1i**, **1j**, and **1k** were treated with **2d**, the expected products **3r**, **3s**, and **3t** were obtained in 90, 92, and 95% yields, respectively (Entries 17, 18, and 19). Next, we checked the reactivity of various *N*-(2-aminophenyl)-indoles **1l**–**q** with **2d**. It has been found that groups such as Cl, OR and NO_2 were well tolerated and, thus, indolo[1,2-*a*]-quinoxalines **3u**–**z** were obtained in good to excellent yields (Entries 20–25). The reaction could also be performed with other (2-aminophenyl)arenes in which the pyrrole or indole moiety was exchanged for a different aromatic ring, such as an electron-rich benzene ring. For example, the reaction of **1r** with **2d** and **2a** gave the corresponding product **3aa** and **3ab** in 75 and 72% yields, respectively, as single regioisomers (Entries 26, 27). When (2-aminophenyl)arene **1s**, which does not contain an electron-donating group, was used, the reaction was found to be sluggish, and **3ac** was isolated in only 30% yield (Entry 28). It should be noted that the present reaction is limited to terminal alkynes; internal alkynes are not viable substrates.

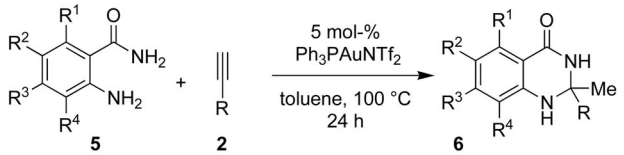
Having established a procedure for hydroamination/hydroarylation of terminal alkynes, we next explored the one-pot cascade reaction between symmetrical diamines and alkynes (Scheme 1). Pleasingly, diamines **4a** and **4b**, on reaction with **2d** under the standard conditions, gave indolo[3,2-*c*]quinolines **3r** and **3s** in 79 and 70% yields, respectively.[28] It is worth mentioning that this multicatalytic[29] process, catalyzed by a single metal catalyst, involves the formation of one C–C bond and two C–N bonds.



Scheme 1. $Ph_3PAuNTf_2$-catalyzed one-pot synthesis of indoloquinolines from **4** and **2d**.

Stimulated by the unique reactivity exhibited by the Gagosz catalyst for hydroamination/hydroarylation of alkynes, we next turned our attention towards double hydroamination reactions. Under the established conditions, several 2-aminobenzamides were treated with aromatic or aliphatic alkynes, and the results are outlined in Table 3. From Entries 1–3 it can be seen that phenylacetylene (**2d**) reacted well with 2-aminobenzamide (**5a**) and its methyl-substituted derivatives **5b** and **5c** to furnish **6a**–**c** in moderate to high yields (70–85%). When halogen-containing substrates, such as **5d**, **5e**, and **5f**, were treated with **2d**, the expected products **6d**, **6e**, and **6f** were obtained in 90, 96, and 75% yields, respectively (Entries 4–6). Other alkynes such as **2b** and **2i** on reaction with **5a** afforded **6g** and **6h** in 98 and 90% yields, respectively (Entries 7 and 8).

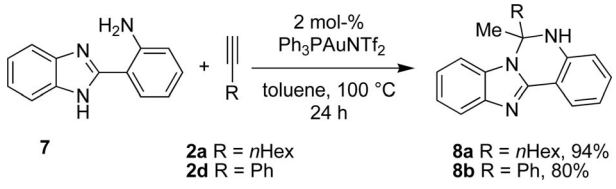
Table 3. $Ph_3PAuNTf_2$-catalyzed double hydroamination of terminal alkynes.[a]



Entry	5	2	6	Yield[b]
1	**5a** $R^1 = R^2 = R^3 = R^4 = H$	**2d**	**6a**	85%
2	**5b** $R^1 = R^2 = R^4 = H$, $R^3 = Me$	**2d**	**6b**	70%
3	**5c** $R^1 = R^3 = H$, $R^2 = R^4 = Me$	**2d**	**6c**	83%
4	**5d** $R^2 = R^3 = R^4 = H$, $R^1 = Cl$	**2d**	**6d**	90%
5	**5e** $R^2 = R^3 = R^4 = H$, $R^1 = F$	**2d**	**6e**	96%[c]
6	**5f** $R^1 = R^3 = R^4 = H$, $R^2 = Br$	**2d**	**6f**	75%
7	**5a**	**2b**	**6g**	98%
8	**5a**	**2i**	**6h**	90%

[a] Reaction conditions: **5** (0.316 mmol), **2** (0.379 mmol), $Ph_3PAuNTf_2$ (5 mol-%), toluene (2 mL), 100 °C, 24 h. [b] Yield of isolated and chromatographically purified material. [c] AgOTf (20 mol-%) was used.

We were pleased to find that not only 2-aminobenzamides **5** but also 2-(2-aminophenyl)benzimidazole (**7**) worked well for the transformation (Scheme 2). The reaction of **7** with **2a** and **2d** under the standard conditions gave benzo[4,5]imidazo[1,2-*c*]quinazolines **8a** and **8b** in 94 and 80% yields, respectively.



Scheme 2. Reaction between 2-(2-aminophenyl)benzimidazole and **2a**/**2d**.

A mechanistic hypothesis based on π-activation catalyzed by $Ph_3PAuNTf_2$ is shown in Figure 2, with substrates **1a** and **2a** as an example. First, coordination of the alkyne to Au^I might take place to generate Au-coordinated alkyne **9**. The formed intermediate **9** would react with **1a** to form Au-coordinated imine **10**, which might be in equilibrium with enamine **10′** or **10′′**. A series of events such as a Fridel–Craft-type reaction, protonation and regeneration of Au catalyst might then occur to afford product **3a**. In short,

the proposed mechanism involves a tandem hydroamination/hydroarylation. Alternative mechanisms involving tandem hydroarylation/hydroamination were ruled out based on the following facts: (1) A control experiment performed with **1a** and **2a** did not show the existence of 2-vinylpyrrole **11**; the presence of starting materials and product **3a** were the only detectable species (Scheme 3); (2) the reaction between *N*-phenylpyrrole **12** and **2a**, under the standard conditions, did not give product **13** – instead, decomposition of **12** was observed (Scheme 4).

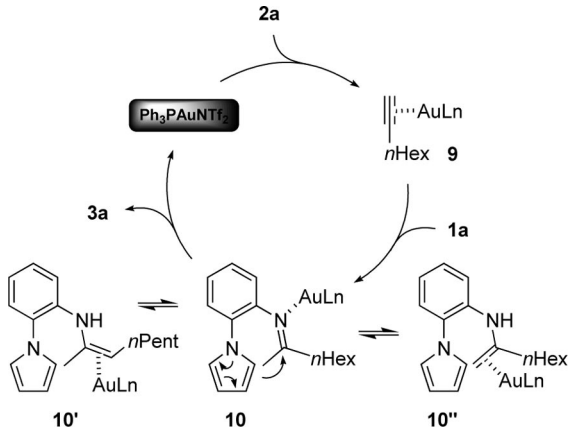
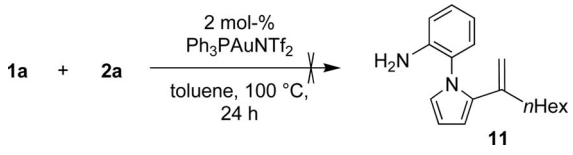
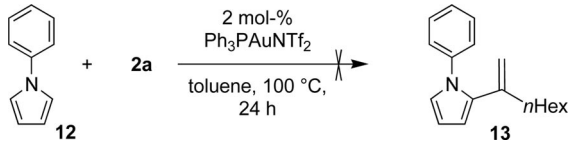


Figure 2. Plausible mechanism exemplified with **1a** and **2a**.



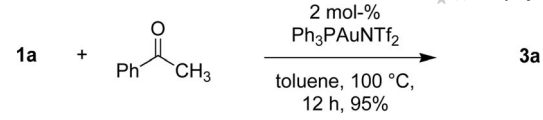
Scheme 3. Reaction between **1a** and **2a** under standard conditions.



Scheme 4. Reaction between *N*-phenylpyrrole **12** and 1-octyne (**2a**).

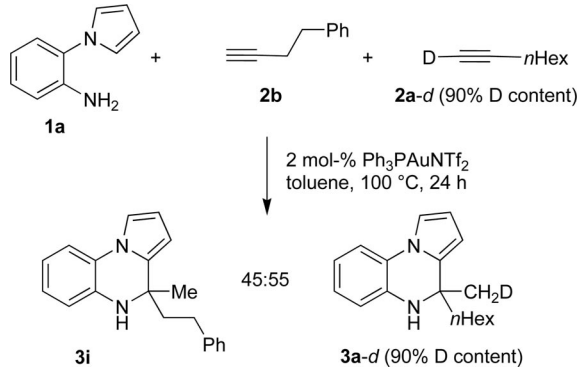
Our proposed mechanism is entirely different to that reported by Yi and Yun.[12] They treated amino-aromatics with terminal alkynes in the presence of $Ru_3(CO)_{12}$ and $HBF_4{\cdot}OEt_2$ in benzene at 90–95 °C and proposed a mechanism involving an intramolecular migratory insertion of amine and subsequent α-pyrrole sp^2 C–H bond activation and cyclization via an unsaturated cationic ruthenium acetylide complex. Due to the strong alkynophilicity of Au catalysts, such C–H bond activation is unlikely to occur in the present case.

To obtain further insight into the mechanism, a reaction between **1a** and acetophenone was conducted in the presence of 2 mol-% $Ph_3PAuNTf_2$ in toluene at 100 °C for 12 h. Product **3a** was obtained in 95% yield, which clearly showed the intermediacy of the imine under the present reaction conditions (Scheme 5).



Scheme 5. Reaction between *N*-(2-aminophenyl)pyrrole (**1a**) and acetophenone.

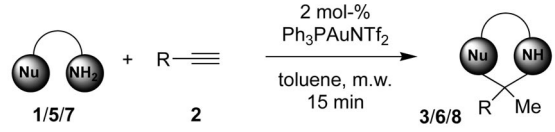
A crossover experiment (Scheme 6) was conducted by treating **1a** (0.126 mmol) with a 1:1 mixture of **2b**/**2a**-*d* (90%) (1 equiv. each) in the presence of 2 mol-% $Ph_3PAuNTf_2$ at 100 °C in toluene. The reaction afforded a 45:55 mixture of **3i**/**3a**-*d* (90% deuterium content) in 92% yield. The unequal ratio of **3i**/**3a**-*d* could arise from a small difference in the rates of reactivity between the differentially substituted alkynes. The observation that the crossover product was not obtained clearly supports the mechanism proposed in Figure 2.



Scheme 6. Crossover experiment.

A significant rate enhancement was observed when the reactions were conducted under microwave conditions.[30] Representative examples are described in Table 4. Reactions of **1a** with **2a** in the presence of 2 mol-% of $Ph_3PAuNTf_2$ under microwave conditions (T = 150 °C, P = 90–110 W) afforded **3a** in 93% yield (Entry 1).[31] It is interesting to note that **1a** reacted with **2d** in the presence of $Ph_3PAuNTf_2$

Table 4. $Ph_3PAuNTf_2$-catalyzed hydroamination/hydroarylation and double hydroamination of terminal alkynes under microwave conditions.[a]



Entry	1/5/7	2	3/6/8	Yield[b]
1	**1a**	**2a**	**3a**	93%
2	**1a**	**2d**	**3k**	91%
3	**5a**	**2d**	**6a**	89%
4	**5a**	**2b**	**6g**	98%
5	**7**	**2a**	**8a**	88%
6	**7**	**2d**	**8b**	90%

[a] Amino-aromatics **1a**/**5a**/**7** (0.316 mmol), alkynes **2** (0.379 mmol), $Ph_3PAuNTf_2$ (2 mol-%), toluene (2 mL), microwaves (m.w.), 150 °C, P = 90–110 W, 15 min (Biotage, Initiator Eight, single-mode reactor). [b] Yield of purified product.

to afford exclusively the desired product **3k** in 91% yield (Entry 2). This is in contrast to our previous results (Table 2, Entry 10), wherein the use of AgOTf as a catalyst was required. The observed difference in the case of the microwave-assisted reaction could be attributed to the faster reaction rate compared with conventional heating, which suppressed the formation of the undesired product.[27] The reaction of **2d** and **2b** with **5a** gave **6a** and **6g** in 89 and 98% yield, respectively (Entries 3 and 4). This microwave-assisted Au^I-catalyzed transformation can be successfully extended to 2-(2-aminophenyl)benzimidazole (**7**), thus leading to the formation of the corresponding benzo[4,5]imidazo[1,2-*c*]quinazolines **8a** and **8b** in 88% and 90% yields, respectively (Entries 5 and 6).

Conclusions

We have developed an efficient $Ph_3PAuNTf_2$-catalyzed direct double hydroamination and hydroamination/hydroarylation of terminal alkynes. Unlike our previously reported methods, tethered hydroxy groups on the alkynes are not necessary, which thereby enlarges the scope of the reaction. These approaches provide a wide range of multisubstituted pyrrolo[1,2-*a*]quinoxalines, indolo[3,2-*c*]quinolines, indolo[1,2-*a*]quinoxalines, tetrahydro-4-quinazolinones, and benzo[4,5]imidazo[1,2-*c*]quinazolines from easily available starting materials. The catalyst loading is relatively low in most cases and the procedure is operationally simple. Furthermore, we have described a $Ph_3PAuNTf_2$-catalyzed one-pot cascade process for the synthesis of indoloquinolines starting directly from symmetrical 2-[2-(2-aminophenyl)-1-ethynyl]anilines and terminal alkynes.

Experimental Section

General Procedure for $Ph_3PAuNTf_2$/AgOTf-Catalyzed Hydroamination/Hydroarylation of Terminal Alkynes: See Table 2. To a screw-cap vial containing a stir bar, were added aromatic amine **1** (0.316 mmol), alkyne **2** (0.379 mmol), and catalyst $Ph_3PAuNTf_2$ (2 mol-% with respect to **1**) or AgOTf (10 mol-% with respect to **1a**) in toluene (2 mL). The reaction vial was fitted with a cap, evacuated and filled with nitrogen. The reaction vial was heated with stirring at 100 °C for the specified time. The reaction mixture was cooled to ambient temperature, diluted with ethyl acetate and filtered through a plug of silica gel. The filtrate was concentrated, and the residue was purified by silica gel column chromatography with hexane/ethyl acetate as an eluent to afford analytically pure product **3**.

4-Hexyl-4-methyl-4,5-dihydropyrrolo[1,2-*a*]quinoxaline (3a): Yield: 76 mg (90%); liquid; R_f = 0.62 (hexane/EtOAc = 90:10). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.26–7.24 (m, 1 H), 7.09–7.08 (m, 1 H), 6.90 (dt, J = 8.1, 1.6 Hz, 1 H), 6.75 (dt, J = 8.1, 1.6 Hz, 1 H), 6.64 (d, J = 7.2 Hz, 1 H), 6.23 (t, J = 3.2 Hz, 1 H), 5.90 (dd, J = 3.2, 1.6 Hz, 1 H), 1.51 (s, 3 H), 1.46–1.24 (m, 10 H), 0.87 (t, J = 6.8 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 135.2, 131.2, 124.6, 118.6, 115.3, 114.4, 113.6, 109.9, 109.7, 102.9, 54.1, 41.9, 31.7, 29.4, 27.1, 24.2, 22.5, 13.9 ppm. IR (film): $\tilde{\nu}_{max}$ = 3360, 3040, 2943, 2930, 2860, 1708, 1615, 1600, 1520, 1460, 1423, 1365, 1160, 970, 850, 740, 725, 704 cm^{-1}. HRMS: calcd. for $C_{18}H_{25}N_2$ [M^+ + H] 269.2018; found 269.2022.

4-Hexyl-4,8-dimethyl-4,5-dihydropyrrolo[1,2-*a*]quinoxaline (3b): Yield: 78 mg (87%); viscous liquid; R_f = 0.63 (hexane/EtOAc = 90:10). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.04 (s, 2 H), 6.68 (d, J = 6.8 Hz, 1 H), 6.52 (d, J = 8.3 Hz, 1 H), 6.18 (t, J = 3.0 Hz, 1 H), 5.85 (dd, J = 3.0, 1.5 Hz, 1 H), 2.29 (s, 3 H), 1.45 (s, 3 H), 1.29–1.20 (m, 10 H), 0.84 (t, J = 6.8 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 132.8, 125.0, 115.3, 115.0, 113.5, 109.6, 102.8, 101.3, 53.9, 41.6, 31.7, 29.5, 26.9, 24.2, 22.5, 20.8, 13.9 ppm. IR (film): $\tilde{\nu}_{max}$ = 3350, 3103, 3022, 2955, 2929, 2856, 1660, 1623, 1597, 1519, 1482, 1419, 1375, 1334, 1285, 1032, 857, 806, 773, 706, 697 cm^{-1}. HRMS: calcd. for $C_{19}H_{27}N_2$ [M^+ + H] 283.2174; found 283.2170.

8-Chloro-4-hexyl-4-methyl-4,5-dihydropyrrolo[1,2-*a*]quinoxaline (3c): Yield: 79 mg (83%); thick liquid; R_f = 0.54 (hexane/EtOAc = 90:10). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.21 (d, J = 1.8 Hz, 1 H), 7.02 (dd, J = 2.8, 1.3 Hz, 1 H), 6.86 (dd, J = 8.3, 2.3 Hz, 1 H), 6.56 (d, J = 8.3 Hz, 1 H), 6.23 (t, J = 3.2 Hz, 1 H), 5.90 (dd, J = 3.2, 1.5 Hz, 1 H), 3.72 (br. s, 1 H), 1.47 (s, 3 H), 1.24–1.20 (m, 10 H), 0.84 (t, J = 6.6 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 135.9, 133.9, 133.3, 124.2, 115.9, 114.5, 113.7, 110.3, 103.4, 101.9, 54.0, 41.9, 31.6, 29.4, 27.0, 24.1, 22.5, 13.9 ppm. IR (film): $\tilde{\nu}_{max}$ = 3350, 3080, 2960, 2958, 2938, 2860, 1611, 1493, 1460, 1380, 1092, 1039, 848, 750, 692, 610 cm^{-1}. HRMS: calcd. for $C_{18}H_{24}ClN_2$ [M^+ + H] 303.1628; found 303.1615.

7,9-Dichloro-4-hexyl-4-methyl-4,5-dihydropyrrolo[1,2-*a*]quinoxaline (3d): Yield: 72 mg (75%); viscous liquid; R_f = 0.57 (hexane/EtOAc = 90:10). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.85 (d, J = 1.5 Hz, 1 H), 6.83 (d, J = 2.3 Hz, 1 H), 6.67 (d, J = 2.1 Hz, 1 H), 6.19 (t, J = 3.4 Hz, 1 H), 5.88 (d, J = 2.1 Hz, 1 H), 3.90 (br. s, 1 H), 1.46 (s, 3 H), 1.31–1.21 (m, 10 H), 0.85 (t, J = 6.8 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 139.2, 134.8, 132.0, 122.3, 122.0, 121.1, 118.9, 114.1, 109.3, 102.6, 53.6, 40.6, 31.7, 29.4, 25.9, 24.2, 22.6, 14.1 ppm. IR (film): $\tilde{\nu}_{max}$ = 3353, 3098, 2963, 2943, 2920, 2874, 1600, 1518, 1490, 1450, 1328, 1050, 887, 844, 750, 707, 690, 605 cm^{-1}. HRMS: calcd. for $C_{18}H_{23}Cl_2N_2$ [M^+ + H] 337.1238; found 337.1227.

Methyl 4-Hexyl-4-methyl-4,5-dihydropyrrolo[1,2-*a*]quinoxaline-8-carboxylate (3e): Yield: 74 mg (72%); light-yellow solid; m.p. 118–120 °C; R_f = 0.45 (hexane/EtOAc = 90:10). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.91 (d, J = 2.2 Hz, 1 H), 7.60 (dd, J = 8.3, 2.2 Hz, 1 H), 7.17 (dd, J = 3.0, 1.5 Hz, 1 H), 6.60 (d, J = 8.3 Hz, 1 H), 6.23 (t, J = 3.7 Hz, 1 H); 5.89 (dd, J = 3.0, 1.5 Hz, 1 H), 4.09 (br. s, 1 H), 3.88 (s, 3 H), 1.51 (s, 3 H), 1.48–1.19 (m, 10 H), 0.83 (t, J = 6.8 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.9, 139.7, 132.5, 126.9, 123.8, 119.5, 115.7, 113.9, 110.4, 103.5, 54.6, 51.8, 43.3, 31.7, 29.4, 28.1, 24.2, 22.5, 14.0 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 3328, 3070, 3050, 2960, 2943, 2850, 1910, 1745, 1603, 1480, 1479, 1463, 1250, 1080, 1050, 977, 845, 775, 742 cm^{-1}. HRMS: calcd. for $C_{20}H_{27}N_2O_2$ [M^+ + H] 327.2073; found 327.2063.

4-Hexyl-4,6-dimethyl-4,5-dihydropyrrolo[1,2-*a*]quinoxaline (3f): Yield: 58 mg (65%); liquid; R_f = 0.72 (hexane/EtOAc = 90:10). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.21 (dd, J = 3.0, 1.5 Hz, 1 H), 6.80 (t, J = 7.5 Hz, 1 H), 6.60 (d, J = 7.5 Hz, 1 H), 6.52 (d, J = 7.5 Hz, 1 H), 6.18 (t, J = 3.0 Hz, 1 H), 5.87 (dd, J = 3.0, 1.5 Hz, 1 H), 3.64 (br. s, 1 H), 2.60 (s, 3 H), 1.44 (s, 3 H), 1.29–1.19 (m, 10 H), 0.84 (t, J = 6.8 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 137.2, 125.7, 124.5, 123.2, 118.5, 114.1, 108.7, 101.7, 53.3, 40.2, 31.8, 29.6, 25.9, 24.3, 22.7, 21.6, 14.2 ppm. IR (film): $\tilde{\nu}_{max}$ = 3350, 3095, 3054, 2956, 2929, 2855, 1597, 1502, 1491, 1415, 1376, 1297, 1164, 1093,

886, 771, 707, 701, 611 cm^{-1}. HRMS: calcd. for $C_{19}H_{27}N_2$ [M$^+$ + H] 283.2174; found 283.2180.

4-Hexyl-4-methyl-4,5-dihydropyrrolo[1,2-*a*]quinoxalin-7-yl Methyl Ether (3g): Yield: 84 mg (89%); light-yellow solid; m.p. 118–120 °C; R_f = 0.48 (hexane/EtOAc = 90:10). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.12 (d, J = 8.3 Hz, 1 H), 6.98 (dd, J = 3.0, 1.5 Hz, 1 H), 6.28–6.24 (m, 1 H), 6.17 (dd, J = 6.8, 3.0 Hz, 2 H), 5.84 (dd, J = 3.7, 1.5 Hz, 1 H), 3.74 (s, 3 H), 3.63 (br. s, 1 H), 1.46 (s, 3 H), 1.33–1.21 (m, 10 H), 0.84 (t, J = 6.8 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.1, 136.5, 130.9, 119.4, 115.0, 113.2, 109.5, 103.3, 102.5, 101.2, 55.2, 54.2, 42.2, 31.8, 29.6, 27.4, 24.3, 22.6, 14.2 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 3347, 3012, 3002, 2979, 1609, 1583, 1510, 1472, 1462, 1334, 1248, 1179, 1031, 829, 751, 743, 704, 691 cm^{-1}. HRMS: calcd. for $C_{19}H_{27}N_2O$ [M$^+$ + H] 299.2123; found 299.2132.

8-Fluoro-4-hexyl-4-methyl-4,5-dihydropyrrolo[1,2-*a*]quinoxaline (3h): Yield: 43 mg (48%); viscous liquid; R_f = 0.68 (hexane/EtOAc = 90:10). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.41 (dd, J = 8.8, 4.9 Hz, 1 H), 6.43–6.33 (m, 3 H), 6.01 (d, J = 2.9 Hz, 1 H), 5.78 (d, J = 3.9 Hz, 1 H), 3.65 (br. s, 1 H), 1.43 (s, 3 H), 1.29–1.21 (m, 10 H), 0.85 (t, J = 6.8 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.4, 132.8, 128.3, 124.6, 121.3, 115.2, 115.0, 113.5, 109.7, 104.4, 102.9, 102.2, 101.8, 54.3, 42.2, 31.6, 29.4, 27.2, 24.2, 22.5, 13.9 ppm. IR (film): $\tilde{\nu}_{max}$ = 3356, 3049, 2957, 2928, 2856, 1705, 1622, 1525, 1493, 1467, 1377, 1278, 1159, 1104, 996, 883, 770, 630 cm^{-1}. HRMS: calcd. for $C_{18}H_{24}FN_2$ [M$^+$ + H] 287.1924; found 287.1911.

4-Methyl-4-phenethyl-4,5-dihydropyrrolo[1,2-*a*]quinoxaline (3i): Yield: 68 mg (75%); liquid; R_f = 0.48 (hexane/EtOAc = 90:10). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.25–7.13 (m, 3 H), 7.12–7.02 (m, 4 H), 6.87 (dt, J = 7.5, 1.5 Hz, 1 H), 6.73 (dt, J = 7.5, 1.5 Hz, 1 H), 6.56 (dd, J = 7.5, 1.5 Hz, 1 H), 6.22 (t, J = 3.7 Hz, 1 H), 5.95 (dd, J = 3.0, 1.5 Hz, 1 H), 2.69–2.57 (m, 2 H), 2.19–2.05 (m, 1 H), 1.98–1.88 (m, 1 H), 1.55 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 142.0, 132.8, 128.8, 128.3, 128.2, 125.7, 124.7, 118.7, 118.1, 115.4, 114.4, 113.8, 109.9, 103.1, 54.3, 43.9, 31.0, 27.7 ppm. IR (film): $\tilde{\nu}_{max}$ = 3359, 3040, 2949, 2927, 2860, 1708, 1612, 1600, 1490, 1473, 1336, 770, 739, 690 cm^{-1}. HRMS: calcd. for $C_{20}H_{21}N_2$ [M$^+$ + H] 289.1705; found 289.1716.

(4-Methyl-4,5-dihydropyrrolo[1,2-*a*]quinoxalin-4-yl)methanol (3j): Yield: 45 mg (67%); white solid; m.p. 138–140 °C; R_f = 0.33 (hexane/EtOAc = 90:10). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.23 (t, J = 7.7 Hz, 1 H), 7.10 (s, 1 H), 6.89 (t, J = 7.7 Hz, 1 H), 6.75 (t, J = 7.7 Hz, 1 H), 6.68 (d, J = 7.7 Hz, 1 H), 6.23 (t, J = 2.8 Hz, 1 H), 5.97 (d, J = 1.9 Hz, 1 H), 3.55 (ABq, J = 10.6 Hz, 2 H), 1.53 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 134.6, 124.8, 118.9, 115.8, 114.4, 114.1, 113.9, 113.8, 110.1, 104.1, 67.9, 54.9, 23.7 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 3356, 3335, 3020, 2960, 2800, 1998, 1620, 1600, 1493, 1456, 1290, 1052, 850, 740, 430 cm^{-1}. HRMS: calcd. for $C_{13}H_{13}N_2O$ [M$^+$ – H] 213.1028; found 213.1039.

4-Methyl-4-phenyl-4,5-dihydropyrrolo[1,2-*a*]quinoxaline (3k): Yield: 80 mg (97%); viscous liquid; R_f = 0.48 (hexane/EtOAc = 90:10). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.27–7.15 (m, 5 H), 7.13–7.07 (m, 2 H), 6.86 (dt, J = 7.5, 1.5 Hz, 1 H), 6.74–6.65 (m, 2 H), 6.23 (t, J = 3.0 Hz, 1 H), 5.94 (dd, J = 3.0, 1.5 Hz, 1 H), 1.85 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 132.9, 128.1, 126.8, 125.6, 124.6, 119.2, 115.7, 114.1, 109.9, 104.5, 56.8, 29.3 ppm. IR (film): $\tilde{\nu}_{max}$ = 3320, 3100, 2942, 1918, 1643, 1605, 1489, 1459, 1320, 1229, 1058, 850, 740, 704 cm^{-1}. HRMS: calcd. for $C_{18}H_{17}N_2$ [M$^+$ + H] 261.1392; found 261.1402.

4-(4-Methoxyphenyl)-4-methyl-4,5-dihydropyrrolo[1,2-*a*]quinoxaline (3l): Yield: 46 mg (50%); viscous liquid; R_f = 0.31 (hexane/EtOAc = 90:10). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.22–7.15 (m, 3 H), 7.08 (s, 1 H), 6.86 (dt, J = 7.5, 1.5 Hz, 1 H), 6.75–6.64 (m, 4 H), 6.22 (t, J = 3.1 Hz, 1 H), 5.89–5.88 (m, 1 H), 4.16 (br. s, 1 H), 3.70 (s, 3 H), 1.82 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.3, 137.9, 134.5, 133.1, 126.9, 125.8, 124.6, 119.7, 116.1, 114.6, 114.2, 113.4, 109.9, 105.5, 56.7, 55.1, 28.9 ppm. IR (film): $\tilde{\nu}_{max}$ = 3328, 3054, 2959, 1707, 1627, 1480, 1432, 1240, 1030, 774, 743, 692, 608 cm^{-1}. HRMS: calcd. for $C_{19}H_{19}N_2O$ [M$^+$ + H] 291.1497; found 291.1493.

3-(4-Methyl-4,5-dihydropyrrolo[1,2-*a*]quinoxalin-4-yl)phenol (3n): Yield: 68 mg (78%); liquid; R_f = 0.24 (hexane/EtOAc = 90:10). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.16 (dd, J = 7.7, 1.1 Hz, 1 H), 7.06 (dd, J = 2.8, 1.3 Hz, 1 H), 6.99 (t, J = 7.9 Hz, 1 H), 6.81 (dt, J = 7.5, 1.1 Hz, 1 H), 6.75–6.59 (m, 4 H), 6.49 (dd, J = 8.1, 2.4 Hz, 1 H), 6.22 (t, J = 3.2 Hz, 1 H), 5.96–5.94 (m, 1 H), 1.78 (s, 3 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 156.7, 148.7, 136.1, 132.5, 128.4, 124.6, 124.3, 117.4, 116.1, 115.1, 114.1, 113.9, 113.1, 112.9, 109.5, 103.6, 55.9, 29.2 ppm. IR (film): $\tilde{\nu}_{max}$ = 3369, 3358, 3057, 2958, 1907, 1598, 1497, 1458, 1220, 1054, 810, 750, 648 cm^{-1}. HRMS: calcd. for $C_{18}H_{17}N_2O$ [M$^+$ + H] 277.1341; found 277.1331.

3-(4-Methyl-4,5-dihydropyrrolo[1,2-*a*]quinoxalin-4-yl)aniline (3o): Yield: 60 mg (67%); yellow solid; m.p. 120–122 °C; R_f = 0.43 (hexane/EtOAc = 85:15). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.26–7.16 (m, 1 H), 7.08–7.07 (m, 1 H), 6.96 (t, J = 7.7 Hz, 1 H), 6.85 (dt, J = 7.5, 1.3 Hz, 1 H), 6.77–6.64 (m, 3 H), 6.48 (s, 1 H), 6.38 (d, J = 7.7 Hz, 1 H), 6.23 (t, J = 3.0 Hz, 1 H), 5.94 (d, J = 2.0 Hz, 1 H), 3.48 (br. s, 3 H), 1.81 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 147.7, 146.0, 135.2, 132.9, 129.3, 129.0, 124.6, 119.0, 115.8, 115.6, 114.5, 114.1, 113.7, 113.0, 109.8, 104.5, 56.7, 29.2 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 3399, 3280, 3100, 1699, 1607, 1550, 1495, 1440, 1350, 1210, 1050, 852, 750, 703 cm^{-1}. HRMS: calcd. for $C_{18}H_{18}N_3$ [M$^+$ + H] 276.1501; found 276.1501.

4-Cyclohexyl-4-methyl-4,5-dihydropyrrolo[1,2-*a*]quinoxaline (3p): Yield: 79 mg (94%); viscous liquid; R_f = 0.69 (hexane/EtOAc = 90:10). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.21–7.18 (m, 1 H), 7.05 (s, 1 H), 6.85 (t, J = 7.7 Hz, 1 H), 6.68 (t, J = 7.5 Hz, 1 H), 6.58 (d, J = 7.7 Hz, 1 H), 6.19 (t, J = 2.8 Hz, 1 H), 5.86 (d, J = 1.8 Hz, 1 H), 3.86 (br. s, 1 H), 1.78–1.59 (m, 5 H), 1.46 (s, 3 H), 1.14–0.84 (m, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 135.3, 132.6, 124.5, 117.9, 114.5, 114.1, 113.9, 113.4, 109.4, 104.2, 56.4, 47.1, 35.4, 27.6, 26.9, 26.4, 26.2, 23.5 ppm. IR (film): $\tilde{\nu}_{max}$ = 3356, 3057, 2953, 2930, 2850, 1708, 1640, 1600, 1495, 1472, 1303, 1049, 745, 705, 430 cm^{-1}. HRMS: calcd. for $C_{18}H_{23}N_2$ [M$^+$ + H] 267.1861; found 267.1863.

4-Methyl-4-(2-pyridyl)-4,5-dihydropyrrolo[1,2-*a*]quinoxaline (3q): Yield: 44 mg (53%); white solid; m.p. 70–72 °C; R_f = 0.27 (hexane/EtOAc = 90:10). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.49 (d, J = 4.5 Hz, 1 H), 7.48–7.36 (m, 2 H), 7.17–7.16 (m, 2 H), 7.01–6.96 (m, 1 H), 6.89–6.77 (m, 3 H), 6.33 (t, J = 3.0 Hz, 1 H), 6.21 (dd, J = 3.7, 1.5 Hz, 1 H), 5.29 (br. s, 1 H), 1.88 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.7, 145.4, 136.4, 129.9, 127.8, 125.2, 124.6, 121.8, 120.7, 119.2, 116.4, 114.3, 110.0, 107.6, 105.7, 57.8, 28.2 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 3340, 3080, 3057, 2959, 1612, 1598, 1448, 1430, 1426, 1050, 1016, 749, 740, 704 cm^{-1}. HRMS: calcd. for $C_{17}H_{15}N_3Na$ [M$^+$ + Na] 284.1164; found 284.1154.

6-Methyl-6-phenyl-6,11-dihydro-5*H*-indolo[3,2-*c*]quinoline (3r): Yield: 88 mg (90%); pale-yellow solid; m.p. 98–100 °C; R_f = 0.46 (hexane/EtOAc = 90:10). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.12 (br. s, 1 H), 7.61 (d, J = 7.3 Hz, 2 H), 7.29–7.23 (m, 3 H), 7.19 (t, J = 7.3 Hz, 2 H), 7.03–6.95 (m, 2 H), 6.88 (d, J = 8.0 Hz, 1 H), 6.83 (t, J = 7.3 Hz, 1 H), 6.64 (t, J = 7.3 Hz, 1 H), 6.48 (d, J = 8.0 Hz, 1 H), 2.07 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ =

147.9, 142.5, 137.1, 130.2, 128.6, 128.1, 126.9, 126.5, 125.6, 121.8, 120.0, 119.9, 119.3, 117.1, 114.2, 113.3, 110.9, 59.1, 29.0 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 3409, 3053, 3022, 2965, 2922, 1623, 1607, 1573, 1509, 1460, 1319, 1135, 1027, 921, 844, 704, 697, 607, 465 cm^{-1}. HRMS: calcd. for $C_{22}H_{19}N_2$ [M^+ + H] 311.1548; found 311.1535.

2,6,8-Trimethyl-6-phenyl-6,11-dihydro-5*H*-indolo[3,2-*c*]quinoline (3s): Yield: 98 mg (92%); white solid; m.p. 208–210 °C; R_f = 0.53 (hexane/EtOAc = 90:10). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.01 (br. s, 1 H), 7.55 (d, J = 7.9 Hz, 2 H), 7.25 (t, J = 7.0 Hz, 2 H), 7.16 (t, J = 7.0 Hz, 1 H), 7.10 (d, J = 7.9 Hz, 1 H), 6.97 (s, 1 H), 6.82 (d, J = 7.9 Hz, 1 H), 6.76 (d, J = 7.9 Hz, 1 H), 6.71 (s, 1 H), 6.38 (d, J = 7.9 Hz, 1 H), 2.24 (s, 3 H), 2.23 (s, 3 H), 2.05 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 147.1, 141.0, 135.4, 129.4, 129.0, 128.0, 126.7, 126.3, 123.3, 120.5, 119.1, 113.9, 113.7, 113.3, 110.5, 61.7, 29.6, 28.9, 21.5 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 3227, 3049, 2921, 2916, 1616, 1556, 1515, 1445, 1310, 1216, 1028, 795, 632 cm^{-1}. HRMS: calcd. for $C_{24}H_{23}N_2$ [M^+ + H] 339.1861; found 339.1877.

2,8-Dichloro-6-methyl-6-phenyl-6,11-dihydro-5*H*-indolo[3,2-*c*]-quinoline (3t): Yield: 114 mg (95%); pale-yellow solid; m.p. 120–122 °C; R_f = 0.46 (hexane/EtOAc = 90:10). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.10 (br. s, 1 H), 7.49 (d, J = 8.8 Hz, 2 H), 7.25 (t, J = 7.0 Hz, 2 H), 7.19–7.12 (m, 3 H), 6.96–6.89 (m, 2 H), 6.79 (s, 1 H), 6.38 (s, 1 H), 2.01 (s, 3 H) ppm. ^{13}C NMR (100 MHz, [D_6]-DMSO): δ = 149.7, 148.8, 142.5, 135.8, 131.1, 128.1, 127.9, 126.5, 125.7, 123.7, 121.3, 120.7, 119.1, 117.8, 114.3, 113.9, 113.0, 112.7, 58.2, 29.1 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 3391, 2921, 1605, 1567, 1506, 1462, 1371, 1295, 1180, 1068, 943, 857, 797, 766, 703, 594 cm^{-1}. HRMS: calcd. for $C_{22}H_{15}Cl_2N_2$ [M^+ – H] 377.0612; found 377.0626.

6-Methyl-6-phenyl-5,6-dihydroindolo[1,2-*a*]quinoxaline (3u): Yield: 94 mg (96%); pale-yellow solid; m.p. 76–78 °C; R_f = 0.59 (hexane/EtOAc = 90:10). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.95 (d, J = 7.5 Hz, 1 H), 7.79 (dd, J = 7.5, 1.5 Hz, 1 H), 7.56 (d, J = 6.8 Hz, 1 H), 7.33–7.29 (m, 2 H), 7.22–7.09 (m, 5 H), 6.94–6.84 (m, 2 H), 6.77 (dd, J = 7.5, 2.2 Hz, 1 H), 6.32 (s, 1 H), 1.92 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.4, 136.3, 131.7, 131.2, 129.7, 128.8, 128.6, 128.5, 128.0, 124.8, 122.1, 120.9, 120.0, 116.3, 110.7, 103.0, 59.3, 20.2 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 3444, 3360, 3054, 2916, 1624, 1603, 1515, 1459, 1332, 1213, 1130, 1009, 884, 827, 762, 746, 617 cm^{-1}. HRMS: calcd. for $C_{22}H_{19}N_2$ [M^+ + H] 311.1548; found 311.1536.

8-Methoxy-6-methyl-6-phenyl-5,6-dihydroindolo[1,2-*a*]quinoxaline (3v): Yield: 105 mg (98%); pale-yellow solid; m.p. 130–132 °C; R_f = 0.59 (hexane/EtOAc = 90:10). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.76 (dd, J = 7.5, 1.5 Hz, 1 H), 7.56 (d, J = 8.3 Hz, 1 H), 7.31–7.29 (m, 2 H), 7.22–7.08 (m, 4 H), 6.94–6.82 (m, 2 H), 6.78 (dd, J = 7.5, 1.5 Hz, 1 H), 6.55 (d, J = 8.3 Hz, 1 H), 6.49 (s, 1 H), 3.94 (s, 3 H), 1.91 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.3, 145.0, 136.3, 128.5, 128.2, 128.0, 127.1, 126.0, 125.6, 124.2, 123.3, 119.8, 116.9, 116.5, 105.3, 104.0, 100.9, 95.9, 64.5, 55.4, 29.2 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 3360, 3056, 2927, 2836, 1599, 1577, 1557, 1436, 1361, 1254, 1184, 1085, 990, 761, 642 cm^{-1}. HRMS: calcd. for $C_{23}H_{21}N_2O$ [M^+ + H] 341.1654; found 341.1655.

9-(Benzyloxy)-6-methyl-6-phenyl-5,6-dihydroindolo[1,2-*a*]quinoxaline (3w): Yield: 98 mg (75%); thick liquid; R_f = 0.51 (hexane/EtOAc = 90:10). ^{1}H NMR (500 MHz, [D_6]DMSO): δ = 7.83–7.79 (m, 1 H), 7.66–7.62 (m, 1 H), 7.46–7.41 (m, 2 H), 7.36–7.24 (m, 5 H), 7.17–7.04 (m, 4 H), 6.99–6.93 (m, 1 H), 6.89–6.85 (m, 2 H), 6.81–6.73 (m, 1 H), 6.34–6.32 (m, 1 H), 5.11–5.07 (m, 2 H), 1.88 (s, 3 H) ppm. ^{13}C NMR (100 MHz, [D_6]DMSO): δ = 153.3, 141.3, 137.1, 136.9, 131.3, 129.7, 128.8, 128.5, 127.9, 127.6, 127.3, 127.2, 126.6, 126.5, 125.6, 125.5, 120.6, 118.6, 116.6, 112.4, 112.0, 110.9, 70.3, 57.2, 28.4 ppm. IR (film): $\tilde{\nu}_{max}$ = 3471, 3375, 3209, 3001, 2935, 2840, 1619, 1580, 1504, 1439, 1388, 1256, 1092, 1056, 978, 924, 741, 698 cm^{-1}. HRMS: calcd. for $C_{29}H_{25}N_2O$ [M^+ + H] 417.1967; found 417.1979.

6-Methyl-9-nitro-6-phenyl-5,6-dihydroindolo[1,2-*a*]quinoxaline (3x): Yield: 81 mg (72%); orange solid; m.p. 212–213 °C; R_f = 0.37 (hexane/EtOAc = 90:10). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.52 (s, 1 H), 8.13 (d, J = 8.7 Hz, 1 H), 7.98 (d, J = 8.7 Hz, 1 H), 7.77 (d, J = 7.8 Hz, 1 H), 7.32 (d, J = 8.7 Hz, 2 H), 7.27–7.24 (m, 2 H), 7.19–7.15 (m, 1 H), 7.03 (t, J = 7.8 Hz, 1 H), 6.95–6.90 (m, 1 H), 6.88–6.84 (m, 1 H), 6.50 (s, 1 H), 4.36 (br. s, 1 H), 1.95 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 145.1, 143.9, 142.1, 136.6, 130.0, 128.9, 128.4, 127.5, 125.8, 125.5, 120.1, 117.8, 117.7, 117.1, 116.9, 116.5, 111.4, 105.5, 100.5, 57.5, 28.7 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 3359, 3024, 2922, 2853, 1619, 1599, 1509, 1462, 1343, 1313, 1072, 886, 744, 458 cm^{-1}. HRMS: calcd. for $C_{22}H_{18}N_3O_2$ [M^+ + H] 356.1399; found 356.1394.

2,6-Dimethyl-6-phenyl-5,6-dihydroindolo[1,2-*a*]quinoxaline (3y): Yield: 77 mg (75%); white solid; m.p. 118–120 °C; R_f = 0.33 (hexane/EtOAc = 90:10). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.95 (d, J = 8.3 Hz, 1 H), 7.59–7.55 (m, 2 H), 7.31–7.07 (m, 7 H), 6.72–6.65 (m, 2 H), 6.34 (s, 1 H), 4.09 (br. s, 1 H), 2.33 (s, 3 H), 1.89 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 144.8, 141.4, 133.9, 133.3, 129.5, 128.1, 127.7, 127.3, 127.0, 125.9, 124.5, 122.3, 120.9, 120.7, 117.4, 116.6, 111.7, 98.9, 57.7, 28.9, 21.2 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 3350, 3067, 2950, 1689, 1604, 1480, 1432, 1305, 1050, 1016, 849, 743, 707 cm^{-1}. HRMS: calcd. for $C_{23}H_{21}N_2$ [M^+ + H] 325.1705; found 325.1704.

2-Chloro-6-methyl-6-phenyl-5,6-dihydroindolo[1,2-*a*]quinoxaline (3z): Yield: 73 mg (70%); liquid; R_f = 0.59 (hexane/EtOAc = 90:10). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.90 (d, J = 8.3 Hz, 1 H), 7.75 (d, J = 2.6 Hz, 1 H), 7.56 (d, J = 7.5 Hz, 1 H), 7.29–7.04 (m, 7 H), 6.86 (dd, J = 8.3, 2.2 Hz, 1 H), 6.68–6.65 (d, J = 8.3 Hz, 1 H), 6.35 (s, 1 H), 1.89 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 144.3, 140.8, 134.4, 133.9, 129.6, 128.3, 127.3, 125.8, 124.6, 123.7, 122.8, 121.3, 121.2, 117.3, 116.8, 111.5, 110.9, 99.6, 57.7, 28.9 ppm. IR (film): $\tilde{\nu}_{max}$ = 3365, 3057, 2924, 2853, 1594, 1561, 1500, 1455, 1415, 1362, 1296, 1232, 1090, 1026, 861, 806, 769, 746, 578 cm^{-1}. HRMS: calcd. for $C_{22}H_{18}ClN_2$ [M^+ + H] 345.1159; found 345.1150.

9-Methoxy-6-methyl-6-phenyl-5,6-dihydrophenanthridine (3aa): Yield: 71 mg (75%); liquid; R_f = 0.61 (hexane/EtOAc = 80:20). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.60 (dd, J = 8.3, 1.5 Hz, 1 H), 7.48–7.45 (m, 2 H), 7.27–7.15 (m, 4 H), 7.04 (dt, J = 7.5, 1.5 Hz, 1 H), 6.77–6.74 (m, 1 H), 6.73 (s, 1 H), 6.66–6.62 (m, 1 H), 6.57 (dd, J = 8.3, 1.5 Hz, 1 H), 3.82 (s, 3 H), 1.81 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.6, 147.5, 143.3, 132.7, 131.9, 130.1, 129.0, 128.4, 128.1, 127.8, 126.8, 123.2, 118.5, 115.1, 112.5, 107.4, 59.1, 55.1, 28.7 ppm. IR (film): $\tilde{\nu}_{max}$ = 3332, 3053, 2959, 2928, 1888, 1605, 1493, 1453, 1411, 1371, 1318, 1283, 1224, 1144, 1076, 1026, 855, 757, 696 cm^{-1}. HRMS: calcd. for $C_{21}H_{20}NO$ [M^+ + H] 302.1545; found 302.1551.

6-Hexyl-6-methyl-5,6-dihydro-9-phenanthridinyl Methyl Ether (3ab): Yield: 70 mg (72%); liquid; R_f = 0.69 (hexane/EtOAc = 80:20). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.59 (d, J = 8.3 Hz, 1 H), 7.21–7.20 (m, 1 H), 7.08–7.01 (m, 2 H), 6.76–6.70 (m, 2 H), 6.53 (d, J = 7.5 Hz, 1 H), 3.86 (s, 3 H), 1.49 (s, 3 H), 1.38–1.21 (m, 10 H), 0.85 (t, J = 6.8 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.4, 143.8, 132.5, 132.0, 128.9, 125.2, 123.1, 120.6, 118.1, 114.9, 112.6, 107.4, 55.7, 55.2, 41.9, 31.7, 29.5, 28.1, 24.1, 22.5, 14.0 ppm. IR (film): $\tilde{\nu}_{max}$ = 3369, 2928, 2856, 1710, 1608, 1498, 1458, 1421, 1376,

1304, 1216, 1172, 1039, 863, 812, 747, 628 cm^{-1}. HRMS: calcd. for $C_{21}H_{28}NO$ [M$^+$ + H] 310.2171; found 310.2182.

6-Methyl-6-phenyl-5,6-dihydrophenanthridine (3ac): Yield: 26 mg (30%); liquid; R_f = 0.71 (hexane/EtOAc = 80:20). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.78–7.75 (m, 2 H), 7.42–7.34 (m, 5 H), 7.30–7.22 (m, 3 H), 7.17–7.09 (m, 2 H), 6.76 (dd, J = 7.7, 1.0 Hz, 1 H), 1.95 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.0, 139.8, 139.2, 132.9, 131.6, 130.0, 129.0, 128.9, 128.6, 128.4, 128.0, 127.7, 126.9, 126.4, 123.6, 119.7, 56.7, 26.4 ppm. IR (film): $\tilde{\nu}_{max}$ = 3373, 3057, 2923, 1951, 1810, 1684, 1634, 1592, 1473, 1438, 1365, 1289, 1208, 1077, 742, 695, 574 cm^{-1}. HRMS: calcd. for $C_{20}H_{18}N$ [M$^+$ + H] 272.1439; found 272.1427.

General Procedure for the $Ph_3PAuNTf_2$-Catalyzed One-Pot Synthesis of Indoloquinolines 3 from 4 and 2d: See Scheme 1. A solution of aromatic amine **4** (0.316 mmol) in toluene (2 mL) was treated with alkyne **2d** (0.379 mmol) in the presence of $Ph_3PAuNTf_2$ (2 mol-% with respect to **4**) according to the procedure described for **1**, to afford **3**.

General Procedure for the $Ph_3PAuNTf_2$-Catalyzed Double Hydroamination of Terminal Alkynes: See Table 3 and Scheme 2. A solution of 2-aminobenzamide **5** or 2-(2-aminophenyl)benzimidazole **7** (0.316 mmol) in toluene (2 mL) was treated with alkyne **2** (0.379 mmol) in the presence of $Ph_3PAuNTf_2$ (2–5 mol-% with respect to **5/7**), according to the procedure described for the synthesis of **3** from **1**, to give analytically pure **6** and **8**.

2-Methyl-2-phenyl-1,2,3,4-tetrahydro-4-quinazolinone (6a): Yield: 64 mg (85%); yellow solid; m.p. 214–215 °C (ref.[32] m.p. 225–229 °C); R_f = 0.59 ($CHCl_3$/MeOH = 95:05). ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 8.63 (br. s, 1 H), 7.50 (dd, J = 7.2, 1.7 Hz, 3 H), 7.38 (br. s, 1 H), 7.23 (t, J = 7.2 Hz, 2 H), 7.14 (t, J = 7.3 Hz, 2 H), 6.75 (d, J = 7.9 Hz, 1 H), 6.55 (t, J = 6.9 Hz, 1 H), 1.68 (s, 3 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 163.7, 147.6, 147.1, 133.2, 127.8, 127.2, 126.9, 125.1, 116.7, 114.9, 114.2, 70.1, 30.6 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 3406, 3180, 3050, 3022, 2993, 2936, 2908, 1667, 1614, 1560, 1493, 1445, 1382, 1217, 1151, 1028, 946, 807, 776, 747, 703, 561 cm^{-1}. HRMS: calcd. for $C_{15}H_{15}N_2O$ [M$^+$ + H] 239.1184; found 239.1188.

2,7-Dimethyl-2-phenyl-1,2,3,4-tetrahydro-4-quinazolinone (6b): Yield: 56 mg (70%); white solid; m.p. 194–196 °C; R_f = 0.65 ($CHCl_3$/MeOH = 95:05). ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 8.39 (br. s, 1 H), 7.54 (d, J = 7.3 Hz, 2 H), 7.43 (d, J = 7.9 Hz, 1 H), 7.23 (t, J = 7.2 Hz, 2 H), 7.13 (t, J = 7.2 Hz, 1 H), 6.54 (s, 1 H), 6.37 (d, J = 7.7 Hz, 1 H), 2.23 (s, 3 H), 1.69 (s, 3 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 163.9, 147.7, 147.1, 143.2, 127.9, 127.2, 126.9, 125.1, 118.1, 114.2, 112.7, 70.1, 30.7, 21.3 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 3405, 3168, 3055, 3022, 2983, 2918, 1666, 1620, 1553, 1488, 1446, 1359, 1278, 1212, 1026, 816, 777, 699, 550, 468 cm^{-1}. HRMS: calcd. for $C_{16}H_{17}N_2O$ [M$^+$ + H] 253.1341; found 253.1349.

2,6,8-Trimethyl-2-phenyl-1,2,3,4-tetrahydro-4-quinazolinone (6c): Yield: 70 mg (83%); pale-yellow solid; m.p. 188–190 °C; R_f = 0.56 ($CHCl_3$/MeOH = 95:05). ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 8.67 (br. s, 1 H), 7.46 (d, J = 7.5 Hz, 2 H), 7.24–7.20 (m, 3 H), 7.13 (t, J = 7.2 Hz, 1 H), 6.89 (s, 1 H), 6.44 (br. s, 1 H), 2.20 (s, 3 H), 2.10 (s, 3 H), 1.70 (s, 3 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 164.3, 147.8, 134.9, 127.8, 126.9, 125.3, 125.0, 124.9, 115.6, 70.1, 30.4, 19.9, 17.1 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 3392, 3150, 3080, 2960, 2925, 2910, 1927, 1685, 1600, 1550, 1480, 1446, 1350, 1050, 850, 748, 707 cm^{-1}. HRMS: calcd. for $C_{17}H_{19}N_2O$ [M$^+$ + H] 267.1497; found 267.1496.

5-Chloro-2-methyl-2-phenyl-1,2,3,4-tetrahydro-4-quinazolinone (6d): Yield: 77 mg (90%); pale-yellow solid; m.p. 196–197 °C; R_f = 0.63 ($CHCl_3$/MeOH = 95:05). ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 8.81 (br. s, 1 H), 7.85 (br. s, 1 H), 7.46 (d, J = 7.4 Hz, 2 H), 7.26 (t, J = 7.2 Hz, 2 H), 7.16 (t, J = 7.2 Hz, 1 H), 7.06 (t, J = 7.7 Hz, 1 H), 6.75 (d, J = 8.3 Hz, 1 H), 6.53 (d, J = 7.7 Hz, 1 H); 1.62 (s, 3 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 161.3, 149.8, 147.0, 132.9, 128.5, 128.0, 127.7, 127.1, 125.0, 119.9, 113.8, 111.8, 69.3, 30.5 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 3391, 3198, 3063, 2921, 1665, 1602, 1562, 1492, 1458, 1380, 1358, 1200, 1125, 1029, 926, 856, 794, 704, 581 cm^{-1}. HRMS: calcd. for $C_{15}H_{14}ClN_2O$ [M$^+$ + H] 273.0795; found 273.0785.

5-Fluoro-2-methyl-2-phenyl-1,2,3,4-tetrahydro-4-quinazolinone (6e): Yield: 78 mg (96%); white solid; m.p. 216–218 °C; R_f = 0.52 ($CHCl_3$/MeOH = 95:05). ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 8.44 (br. s, 1 H), 7.47 (m, 3 H), 7.24 (t, J = 7.2 Hz, 2 H), 7.15 (t, J = 7.2 Hz, 1 H), 7.07 (m, 1 H), 6.56 (d, J = 7.8 Hz, 1 H), 6.20 (t, J = 8.5 Hz, 1 H), 1.68 (s, 3 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]-DMSO): δ = 163.8, 161.1, 160.4, 149.5, 147.1, 134.1, 133.9, 131.4, 131.2, 128.0, 127.1, 125.0, 111.6, 110.4, 104.4, 104.1, 101.7, 101.4, 69.8, 30.4 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 3399, 3186, 3055, 2926, 1666, 1625, 1569, 1449, 1371, 1317, 1224, 1205, 1146, 1044, 1028, 799, 783, 750 cm^{-1}. HRMS: calcd. for $C_{15}H_{14}FN_2O$ [M$^+$ + H] 257.1090; found 257.1099.

6-Bromo-2-methyl-2-phenyl-1,2,3,4-tetrahydro-4-quinazolinone (6f): Yield: 75 mg (75%); yellow solid; m.p. 178–180 °C; R_f = 0.63 ($CHCl_3$/MeOH = 95:05). ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 8.83 (br. s, 1 H), 7.69 (br. s, 1 H), 7.57 (d, J = 2.3 Hz, 1 H), 7.47 (d, J = 7.6 Hz, 2 H), 7.25 (t, J = 7.2 Hz, 3 H), 7.16 (t, J = 7.2 Hz, 1 H), 6.73 (d, J = 8.7 Hz, 1 H), 1.67 (s, 3 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 162.5, 147.1, 146.2, 135.7, 129.2, 128.0, 127.2, 125.0, 118.5, 116.7, 107.8, 70.2, 30.4 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 3300, 3156, 3049, 2968, 1901, 1690, 1604, 1545, 1480, 1456, 1050, 749, 658, 448 cm^{-1}. HRMS: calcd. for $C_{15}H_{14}BrN_2O$ [M$^+$ + H] 317.0290; found 317.0282.

2-Methyl-2-phenethyl-1,2,3,4-tetrahydro-4-quinazolinone (6g): Yield: 82 mg (98%); white solid; m.p. 148–150 °C; R_f = 0.66 ($CHCl_3$/MeOH = 95:05). ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 7.77 (s, 1 H), 7.65 (d, J = 7.3 Hz, 1 H), 7.19 (t, J = 7.3 Hz, 2 H), 7.15 (d, J = 7.3 Hz, 2 H), 7.09 (t, J = 7.3 Hz, 1 H), 6.63–6.59 (m, 2 H), 6.14 (br. s, 1 H), 2.79–2.68 (m, 2 H), 2.03–1.91 (m, 2 H), 1.47 (s, 3 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 163.1, 147.1, 141.9, 133.2, 128.3, 128.1, 127.1, 125.6, 116.2, 114.1, 113.5, 68.9, 43.1, 29.8, 28.0 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 3278, 3172, 3023, 2969, 2916, 1644, 1612, 1581, 1511, 1486, 1393, 1155, 1031, 753, 700 cm^{-1}. HRMS: calcd. for $C_{17}H_{19}N_2O$ [M$^+$ + H] 267.1497; found 267.1508.

2-Cyclohexyl-2-methyl-1,2,3,4-tetrahydro-4-quinazolinone (6h): Yield: 69 mg (90%); yellow solid; m.p. 166–168 °C; R_f = 0.63 ($CHCl_3$/MeOH = 95:05). ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 7.60 (d, J = 8.3 Hz, 1 H), 7.38 (br. s, 1 H), 7.12 (t, J = 7.2 Hz, 1 H), 6.61 (d, J = 8.3 Hz, 1 H), 6.56 (t, J = 7.2 Hz, 1 H), 5.94 (br. s, 1 H), 1.86–1.72 (m, 5 H), 1.64–1.57 (m, 2 H), 1.36 (s, 3 H), 1.19–1.02 (m, 4 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 162.8, 146.9, 133.1, 126.9, 115.6, 113.5, 113.4, 71.1, 47.8, 30.6, 26.6, 26.3, 25.9, 25.8, 24.7 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 3336, 3183, 3049, 3022, 2927, 2852, 1634, 1608, 1577, 1506, 1485, 1448, 1330, 1273, 1150, 1047, 803, 769, 752, 594 cm^{-1}. HRMS: calcd. for $C_{15}H_{21}N_2O$ [M$^+$ + H] 245.1654; found 245.1651.

6-Hexyl-6-methyl-5,6-dihydrobenzo[4,5]imidazo[1,2-*c*]quinazoline (8a): Yield: 95 mg (94%); thick liquid; R_f = 0.45 (hexane/EtOAc = 70:30). ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 7.87 (d, J = 7.7 Hz, 1 H), 7.67–7.60 (m, 2 H), 7.24–7.14 (m, 3 H), 6.90 (s, 1 H), 6.78 (d, J = 8.1 Hz, 1 H), 6.72 (t, J = 7.5 Hz, 1 H), 1.85 (s, 3 H), 1.49–

1.01 (m, 10 H), 0.74 (t, J = 6.8 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 147.3, 143.9, 143.3, 132.3, 131.5, 124.5, 121.9, 121.8, 118.8, 117.2, 113.8, 111.7, 110.7, 74.3, 40.2, 30.9, 28.3, 27.4, 22.9, 21.8, 13.7 ppm. IR (film): $\tilde{\nu}_{max}$ = 3356, 3093, 2956, 2927, 2855, 1612, 1600, 1480, 1449, 1310, 1050, 855, 748 cm^{-1}. HRMS: calcd. for $C_{21}H_{26}N_3$ [M$^+$ + H] 320.2127; found 320.2133.

6-Methyl-6-phenyl-5,6-dihydrobenzo[4,5]imidazo[1,2-*c*]quinazoline (8b): Yield: 79 mg (80%); pale-yellow solid; m.p. 148–150 °C (ref.[33] m.p. 148 °C); R_f = 0.52 (hexane/EtOAc = 70:30). ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 8.03 (d, J = 7.7 Hz, 1 H), 7.65–7.55 (m, 4 H), 7.38–7.36 (m, 2 H), 7.18 (dt, J = 7.3, 1.3 Hz, 1 H), 7.10 (t, J = 7.3 Hz, 1 H), 6.90–6.77 (m, 3 H), 6.45–6.42 (m, 1 H), 2.17 (s, 3 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 147.6, 143.8, 143.3, 143.0, 132.9, 131.5, 128.4, 125.7, 124.6, 122.0, 121.8, 118.8, 118.2, 114.6, 111.9, 111.6, 74.8, 26.5 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 3226, 3055, 3022, 2927, 1614, 1588, 1532, 1449, 1477, 1372, 1309, 1270, 1168, 1026, 800, 746, 695 cm^{-1}. HRMS: calcd. for $C_{21}H_{18}N_3$ [M$^+$ + H] 312.1501; found 312.1497.

General Procedure for the $Ph_3PAuNTf_2$-Catalyzed Hydroamination/Hydroarylation and Double Hydroamination of Terminal Alkynes under Microwave-Assisted Conditions: A solution of the amino-aromatic **1**, **5** or **7** (0.316 mmol), alkyne **2** (0.379 mmol) and $Ph_3PAuNTf_2$ (2 mol-%) in toluene (2 mL) was sealed under nitrogen in a reaction vial and irradiated in a microwave reactor (Biotage, initiator 8, single-mode reactor) at 150 °C for 15 min. On cooling the reaction mixture to ambient temperature, the solvent was removed in vacuo, and the black residue was purified by column chromatography (silica gel; EtOAc/hexane, 90:10) to afford pyrrolo[1,2-*a*]quinoxalines **3**/tetrahydro-4-quinazolinones **6**/benzo-[4,5]imidazo[1,2-*c*]quinazolines **8**.

Supporting Information (see footnote on the first page of this article): Preparation of starting materials and copies of ^{1}H and ^{13}C NMR spectra of all newly synthesized products.

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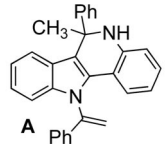

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