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Revisiting the Gold-Catalyzed Dimerization of 2-Ethynylanilines: A Room-Temperature and Silver-Free Protocol for the Synthesis of Multifunctional Quinolines

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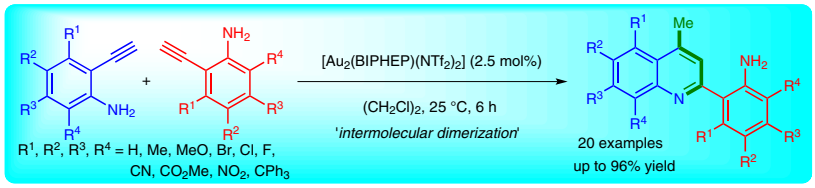
Dedicated to Professors Vèronique Michelet and Virginie Ratovelomanana-Vidal with friendship and respect for their contributions to transition-metal catalysis.



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Abstract A room temperature and silver-free protocol for the formation of quinolines from 2-ethynylanilines through a dimerization event was achieved using a dinuclear gold catalyst, $Au_2(BIPHEP)(NTf_2)_2$. The reaction is inherently modular, allowing for the incorporation of peripheral substituents at any site of the quinoline product. The reaction is readily applied to other heterocyles also as exemplified by the preparation of naphthyridines. Competition reactions to determine the reactivity of dissimilar alkynes demonstrated that the product ratio of dimerization vs intermolecular addition is rather dependent on the electronic nature of aryl substituent on the alkynes. However, control experiments with substrates possessing internal alkynes resulted in cycloisomerization instead of expected dimerization, which is indicative of possible steric influence of the alkyne terminus in the reaction outcome.

Key words 2-ethynylanilines, dimerization, quinolines, atom-economy, dinuclear gold complex, silver-free approach, competition reactions

The last decade has witnessed the upsurge of homogeneous gold catalysis in synthetic chemistry mainly because of its unique ability to activate C≡C bond leading to the evolution of powerful methods to efficiently assemble diverse structures.[1] From what has been learned from the literature, a wide array of gold(I) and gold(III) catalysts with different ligands is commercially available by now or can be readily synthesized at the bench.[2] Practically, the most convenient catalysts are gold complexes [AuLL′]X and [AuLX] with weakly coordinating neutral (L′) or anionic ligands (X), which could enter catalytic cycles by associative ligand exchange with the substrate.[3] The properties of the catalysts can be easily tuned sterically or electronically depending on the ligand.[4] For example, cationic gold(I) species are regarded as the most powerful catalysts for the electrophilic activation of alkynes toward nucleophiles due to the lower LUMO properties and poor back-donation of cationic gold species and behave 'softer' than simple gold(III) salts. They are generally formed in situ via cationization of a gold(I) complex (usually R_3PAuCl) by means of halide abstraction with a silver co-catalyst (AgOTf, $AgNTf_2$, $AgBF_4$, $AgSbF_6$, $AgClO_4$, $AgPF_6$).[5] Early gold complexes featured phosphine ligands predominantly such as PPh_3 and these were joined recently by N-Heterocyclic Carbenes (NHCs). Thanks to their unique electronic and steric properties, carbene ligands offer highly valuable features for gold catalysis.[6] It has been suggested that the selectivity in catalytic applications in Au-NHC systems may very well be controlled as a function of backbone substitutions, flexible N-substituents, and ligand sterics. The main features brought by NHC coordination are thermal stability of the resulting complex and increased electron-donating abilities compared to the ubiquitous tertiary phosphine family. Additionally, they possess unprecedented σ-donation and steric bulk that enhances the stability of catalytic intermediates. Another possibility to use the most active and stable gold catalysts is their ligation with a special class of NHCs called N-Heterocyclic Oxo-Carbenes (NHOCs),[7] Nitrogen Acyclic Carbenes (NACs),[8] and NHC-gold(I) hydroxide complexes ([Au(OH)NHC]).[9] These new generation AuNHCs exhibit improved catalytic activity as compared to the typical gold catalysts and they have been shown to be effective in numerous transformations with quite promising TONs. Towards this end, the development of state-of-the-art gold catalysts continues to emerge in the literature and application towards existing or novel organic transformations becomes highly attractive.

On the other hand, Sakai et al. in their seminal work described the unusual dimerization of 2-ethynylanilines promoted by $InBr_3$[10] (Scheme 1). As part of our research endeavor in gold catalysis,[11] we have previously communicated that the same reaction could be successfully realized using a catalytic quantity of $AuCl_3$ along with AgOTf as co-

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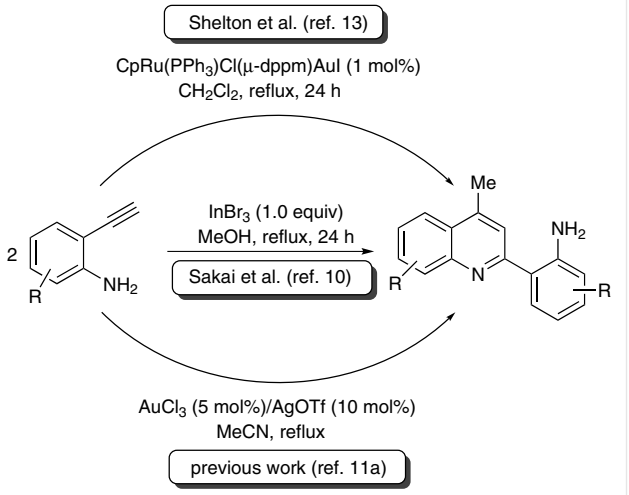
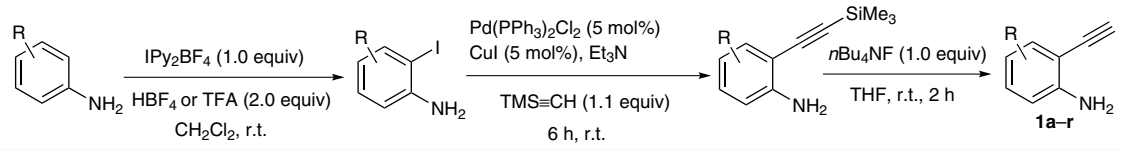


Scheme 1 Dimerization of 2-ethynylanilines

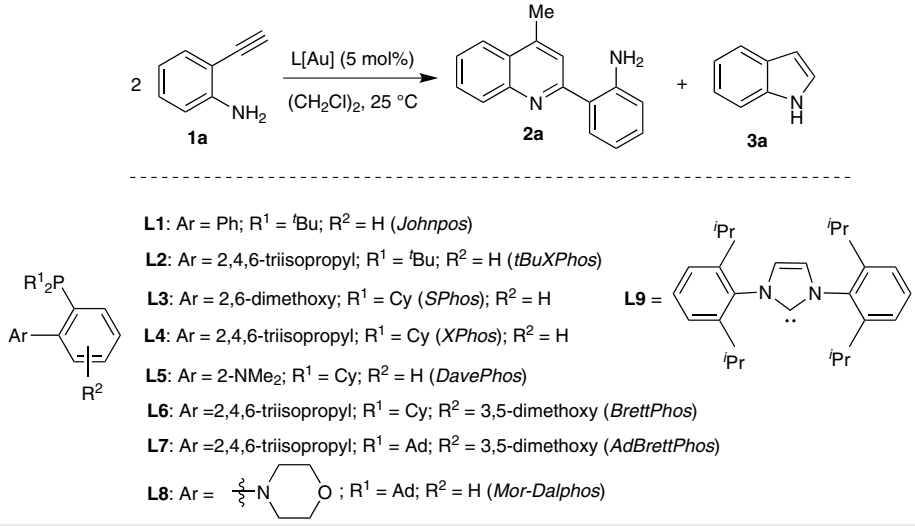
catalyst[11a] (Scheme 1). The Au/Ag catalytic systems allowed, with good to excellent yields, the preparation of a broad variety of quinolines, an important heterocyclic core possessing multifarious medicinal applications.[12] Whilst the former method suffers from the use of stoichiometric quantity of $InBr_3$, the shortcoming of latter is the rather harsh reaction conditions generated by elevated temperature (84 °C) and practical difficulties associated with handling moisture sensitive silver salts limited their synthetic utility. Following our gold-catalyzed protocol, Shelton et al. in 2010 showcased the use of heterobimetallic catalyst of the type $CpRu(PPh_3)Cl(\mu\text{-dppm})AuI$ in this dimerization reaction[13] (Scheme 1). In continuation of our previous communication concerning an original gold(III)/silver(I) based catalytic system allowing the dimerization of a broad range of 2-ethynylaniline substrates, we wish to report herein our endeavors towards the discovery of an efficient dinuclear gold catalytic system with no silver co-catalyst allowing the room temperature dimerization of 2-ethynylanilines.

The synthetic route to the requisite precursors is outlined in Scheme 2. At the outset, various substituted anilines were subjected to Barluenga iodination, which afforded 2-iodoanilines in quantitative yields.[14] Sonogashira coupling of the resulting iodoanilines with trimethylsilylacetylene[15] afforded 2-(trimethylsilylethynyl)anilines, which upon subsequent desilylation under basic condition[16] led to 2-ethynylanilines **1a**–**t**.

We embarked on our search for conditions to perform dimerization reaction drawing precedence from our earlier work, in which $AuCl_3$/AgOTf was used as catalyst and acetonitrile was used as solvent (see, Scheme 1). Several points regarding the optimization of conversion of **1a** to **2a** are worth noting. (i) Solvents like MeOH, EtOH, THF, $MeNO_2$,



Scheme 2 Synthesis of 2-ethynylanilines **1a**–**r**



Scheme 3 Optimization of reaction conditions

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and MeCN were avoided on the basis of their coordinating ability to the catalyst, which could eventually decrease the π-acidity of the catalyst. (ii) Therefore, we preferred to use halogenated solvents and in particular 1,2-dichloroethane, since it offers an additional advantage of performing the reaction at high temperature. (iii) In order to avoid use of the silver co-catalyst, we envisaged to use only the stable gold complexes possessing non-nucleophilic anions. (iv) Simple gold(III) salts are known to cyclize 2-ethynylanilines to indoles;[17] to restrict this side reaction gold(I) catalysts with bulky ligands were screened. Towards this end, the model substrate **1a** (0.5 M/1,2-DCE) was submitted to catalytic amounts (5 mol%) of different gold complexes at 25 °C (Scheme 3). The data presented in Table 1 highlight the key findings of our initial search for the dimerization reaction.

It can be seen there that when **1a** was reacted with Gagosz's catalyst ($Ph_3PAuNTf_2$),[18] the reaction takes place, but the conversion of **1a** to **2a** was too slow to constitute good catalytic system (Table 1, entry 1). *t*-$Bu_3PAuNTf_2$ and $Ph_3PAuOTf$ also proved to be rather ineffective as there is hardly any conversion to **2a** (entries 2 and 3). Given the notable ability to hydroaminate alkynes, Ph_3PAuMe in combination with heteropolyacids was also tested,[19] though decomposition was observed. Switching to gold(I) catalyst having sterically encumbered phosphine ligand such as JohnPos (**L1**), DavePhos (**L5**), and MorDalphos (**L8**) the conversion towards **2a** increased at the expense of **3a** (entries 5, 6, 11, 14, and 15), whereas in the case of *t*-BuxPhos (**L2**), SPhos (**L3**), and BrettPhos (**L6**) most of the starting materials remain unconsumed (entries 7–9 and 12). With XPhos (**L4**) and AdBrettPhos (**L7**), the expected dimerization turned out to be a complete failure with no product being formed (entries 10 and 13). The influence of NHC-ligand was also studied by employing Ipr carbene (**L9**), where it was noticed that the conversion turned only in favor of **3a** (entries 16 and 17). At this point, we investigated the use of chloronium-bridged dinuclear gold catalysts[20] such as $[(Ph_3PAu)_2Cl]BF_4$ and $[(Mes_3PAu)_2Cl]BF_4$ and were pleased to witness a significant amelioration in the formation of **2a** (entries 18 and 19). Encouragingly, the bimetallic gold catalyst possessing BIPHEP ligand[21] showed inferior results in terms of conversion ratio of **2a**:**3a** reaching 71:4 (entry 20). An increase in the reaction temperature using the same catalyst resulted in decreased conversion of **2a** to 52% (entry 21). Much to our delight, by increasing the substrate concentration to 1 M, an almost complete conversion towards **2a** was observed, with an isolated yield of 89% (entry 22). A further improvement was achieved by reducing the catalytic loading to 2.5 mol% to realize a full conversion, thereby furnishing the desired product in 94% yield (entry 23). Finally, the reaction with oxonium bridged trinuclear gold catalyst, $[Ph_3PAu]_3OBF_4$ led to lower conversion of **2a** (entry 24).

Table 1 Catalyst Screening for the Dimerization of **1a**

Entry	L[Au]	Time (h)	**1a**/**2a**/**3a**,[a] yield (%)[b]
1	$Ph_3PAuNTf_2$	24	60/10/30
2	*t*-$Bu_3PAuNTf_2$	24	67/0/33
3	$Ph_3PAuOTf$	24	50/0/50
4	$Ph_3PAuMe/H_3[PW_{12}O_{40}]$	12	degradation[c]
5	**L1**$Au(MeCN)SbF_6$	24	60/28/12
6	**L1**$AuNTf_2$	24	62/30/8
7	**L2**$Au(MeCN)SbF_6$	36	81/10/9
8	**L3**$Au(MeCN)SbF_6$	24	79/9/12
9	**L3**$AuNTf_2$	24	72/13/15
10	**L4**$AuNTf_2$	48	89/0/11
11	**L5**$AuNTf_2$	36	55/28/17
12	**L6**$AuNTf_2$	36	73/7/20
13	**L7**$AuNTf_2$	48	78/0/22
14	**L8**$Au(MeCN)SbF_6$	36	24/31/45
15	**L8**$AuNTf_2$	24	14/33/53
16	**L9**AuOH	48	38/25/37
17	**L9**$Au(MeCN)BF_4$	24	43/16/41
18	$[(Ph_3PAu)_2Cl]BF_4$	24	26/50/24
19	$[(Mes_3PAu)_2Cl]BF_4$	24	24/58/18
20	$Au_2(BIPHEP)(NTf_2)_2$	24	25/71/4
21[d]	$Au_2(BIPHEP)(NTf_2)_2$	2	16/52/32
22[e]	$Au_2(BIPHEP)(NTf_2)_2$	6	4/96/0, 89
23[e,f]	$Au_2(BIPHEP)(NTf_2)_2$	6	0/100/0, 94
24	$[Ph_3PAu]_3OBF_4$	24	21/40/39

[a] Determined by HPLC of the crude reaction mixture.
[b] Isolated yields after column chromatography.
[c] Sevaral unidentified by-products were also detected.
[d] Reaction was performed at reflux.
[e] Reaction performed at 1 M in substrate.
[f] Amount of catalyst used: 2.5 mol%.

Having established the optimal conditions, the scope of the methodology was explored by subjecting a range of 2-ethynylanilines (Scheme 4). Tolerance toward a wide range of functionalities (electron-withdrawing and -releasing groups) on the 2-ethynylaniline was demonstrated by obtaining the corresponding quinolines in moderate to excellent yields (Table 2). It is pertinent to note that substrates having electron releasing groups afforded good to excellent yields of the products (Table 2, entries 1, 2, 7, 8, 10, 17, and 18). In contrast, electron-withdrawing groups led to somewhat lower yields (entries 3-6, 9, 11–13, and 16). This variability in yields observed with respect to the electronic nature of the substituents can be explained by looking at the diminished reactivity of electron-deficient anilines towards hydroamination.[22] The current protocol is amenable to substrates containing peripheral substituents at all positions (R^1, R^2, R^3, and R^4) with respect to the alkyne residue,

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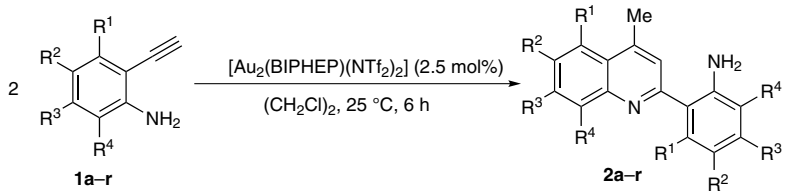


Scheme 4 Dimerization under optimized conditions

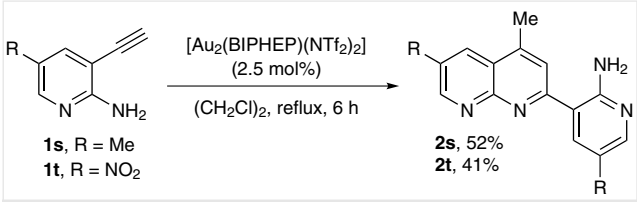
whereas an *ortho*-substitution (R^1) was not reported in previous disclosures.[10,11a,13] The quinolines **2a**–**r** formed were characterized by IR, ^{1}H NMR, ^{13}C NMR, and mass spectroscopy. As an illustrative example, the IR spectrum of compound **2a** exhibited broad peak at 3452 cm^{-1} revealing the presence of NH_2 functionality. The ^{1}H NMR spectra of compound **2a** recorded in $CDCl_3$ showed fourteen protons. A singlet peak at δ_H = 2.74 indicated the presence of aryl-CH_3 protons. The appearance of a broad singlet corresponding to two protons at δ_H = 6.15, indicated the presence of NH_2 group (D_2O exchangeable). In ^{13}C NMR spectra, a peak at δ_C = 19.1 was attributed to the aryl-CH_3 group. Further in mass spectrum, the molecular ion peak (M^+ + 1) appeared at m/z = 235, which is exactly double the value of the corresponding monomer (m/z = 117), confirmed the formation of the product **2a**.

Table 2 Synthesis of Substituted Quinolines **2a**–**r**

Entry	R^1	R^2	R^3	R^4	Product[a]	Yield (%)[b]
1	H	H	H	H	**2a**	94
2	H	Me	H	H	**2b**	89
3	H	F	H	H	**2c**	64
4	H	NO_2	H	H	**2d**	70
5	H	Cl	H	H	**2e**	81
6	H	CN	H	H	**2f**	79
7	H	H	MeO	H	**2g**	87
8	H	Me	Me	H	**2h**	95
9	H	Br	H	Cl	**2i**	73
10	H	Me	H	Me	**2j**	96
11	H	Me	H	Cl	**2k**	77
12	H	Br	H	Br	**2l**	75
13	H	NO_2	H	MeO	**2m**	60
14	H	CO_2Me	H	MeO	**2n**	76
15	H	CPh_3	H	MeO	**2o**	64
16	H	CO_2Me	H	Me	**2p**	74
17	Me	H	H	Me	**2q**	90
18	Me	H	H	H	**2r**	86

[a] Products were characterized by IR and NMR spectroscopy, and mass spectrometry.
[b] Isolated yield after column chromatography.

With the scope towards the synthesis of quinolines explored, our attention was turned to the preparation of 1,8-naphthyridines, a structural motif with pharmacological significance.[23] The synthetic precursors, 2-amino-3-ethynylpyridines **1s** and **1t** were prepared by literature procedure[24] and subsequently subjected to our reaction conditions (Scheme 5). Owing to the high polar nature of **1s** and **1t**, the reaction was performed at reflux temperature to achieve homogenity and found only a moderate yield of the corresponding naphthyridine products **2s** and **2t**.



Scheme 5 Synthesis of 1,8-naphthyridines

We next sought out to operate the gold(I)-catalyzed intermolecular reactivity between two dissimilar alkynes as depicted in Scheme 6. Accordingly, a mixture of 2-ethynylaniline (**1a**) with different terminal alkynes **4a**–**f** in an equimolar ratio was subjected to these reaction conditions. Two main products were isolated, the expected dimerized product **2a** accompanied by the addition product **5a**–**f**.[25] Alkynes of different electronic nature exert a profound effect on the selectivity of competitive dimerization versus intermolecular addition. Interestingly, electron-donating substituents on the phenyl ring (*p*-tolyl **4b**, *p*-anisyl **4c**, and *m*-tolyl **4f**) favor the predominant formation of intermolecular addition products (**5b**, **5c**, and **5f**), whereas electron-withdrawing groups (4-ClC_6H_4 **4d** and 2-ClC_6H_4 **4e**) and hydrogen (**4a**) favor the dimerization products (**5a**, **5d**, and **5e**). This trend can be rationalized in terms of enhancement of electron density at the triple bond by electron-donating substituents, which interacts with Lewis acidic gold(I) catalyst with ease. Such observations are also consistent with the increased reactivity of electron-rich substrates towards dimerization reaction in which high yields were observed (Table 2, entries 1, 2, 7, 8, 10, 17, and 18).

A clue to understand the steric influence of the alkyne residue was gleaned from a study of the gold(I)-catalyzed reaction of substrate possessing internal alkyne such as 2-

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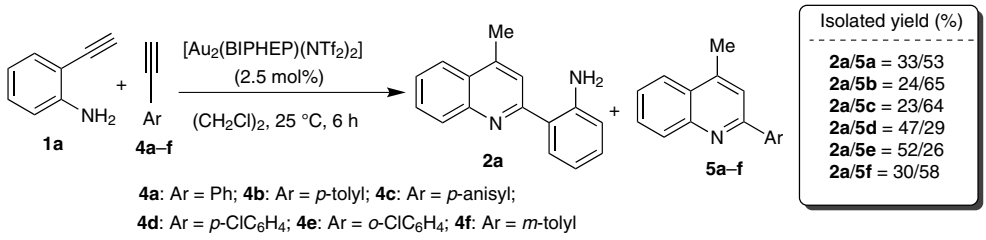
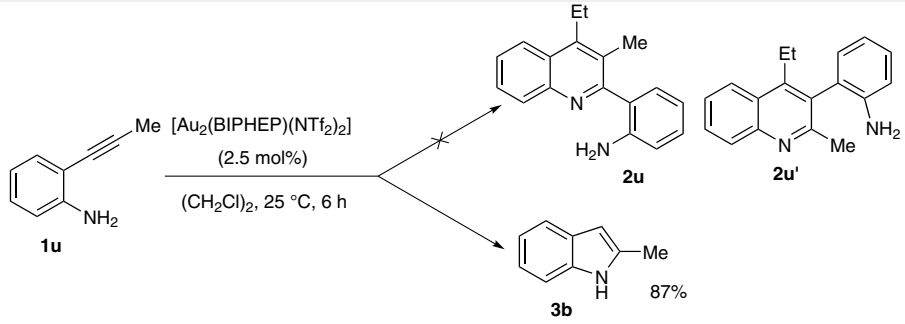


Scheme 6 Gold(I)-catalyzed competitive reactions

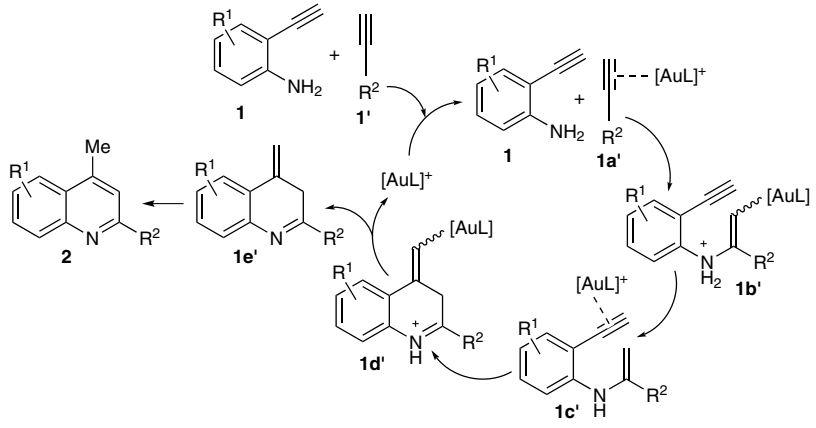


Scheme 7 Control experiment using internal alkyne **1u**

(prop-1-ynyl)aniline (**1u**) (Scheme 7). However, the expected products **2u** and **2u′** were not observed. Conversely, the cycloisomerization product **3b** was formed solely. Although not conclusive, this study suggests that the dimerization process is not induced in more sterically hindered and less reactive internal alkynes and happens to occur only if no substituent is present at the alkyne terminus.

Based on this observation, a plausible mechanistic description for the dimerization process is shown in Scheme 8. According to which, activation of alkyne **1′** by gold(I) forms π-complex **1a′**, which allows the nucleophilic attack of NH_2 group of another alkyne **1** to form vinyl-gold intermediate **1b′**. Species **1b′** undergoes proto-deauration to furnish intermediate **1c′**. The latter is activated by gold(I) again, and a subsequent cyclization occurs to afford the intermediate **1d′**. Proto-deauration of **1d′** regenerates the gold(I) catalyst and delivers **1e′**, which upon proton transposition affords the dimerized product **2**.

Through dimerization of 2-ethynylanilines under the catalysis of dinuclear gold catalyst $Au_2(BIPHEP)(NTf_2)_2$, a room temperature and silver-free synthesis of quinolines was established. This protocol possesses broad substrate scope and the chemical yields are generally good to excellent. Not only limited to quinolines, the methodology is also amenable to the synthesis of structurally related naphthyridines. Reaction between two dissimilar alkynes was also made possible in a competitive mode and two different products (i.e., dimerization and intermolecular addition)



Scheme 8 Tentative mechanism for the dimerization

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can be generated. The product ratio of dimerization versus intermolecular addition is rather dependent on the electronic nature of aryl substituents on the alkynes. Reaction with internal alkyne **1u** offered cycloisomerized product instead of the expected dimerization product. Our future investigation will be towards elucidating the exact reaction mechanism and on the application of this methodology to the synthesis of natural products having pharmacological significance.

All commercially available solvents and reagents were dried and purified by standard purification procedures. Gold complexes were purchased from Sigma-Aldrich and Strem chemicals, USA. Bench stable $Au_2(BIPHEP)(NTf_2)_2$ complex was prepared from $Au_2(BIPHEP)Cl_2$ and $AgNTf_2$ according to the procedure of Bandini et al.[21] Solutions in organic solvents were dried with anhydrous Na_2SO_4. Solvents were evaporated under reduced pressure. Melting points were obtained using open capillaries and are uncorrected. IR spectra were recorded on a PerkinElmer FTIR spectrophotometer as KBr pellets for solid compounds and neat sample for liquid compounds. GC analyses were performed on a Hewlett-Packard 5890 series II instrument connected to a Merck D-2500 or D-2000 integrator with a flame-ionization detector. HPLC analyses were performed on Waters instruments (Waters 486 detector, 717 autosampler equipped with Daicel column (46 mm i.d. × 25 cm). ^1H and ^{13}C NMR spectra were obtained in DMSO-d_6 and $CDCl_3$ on a JEOL spectrometer at 500 and 125 MHz, respectively. Proton chemical shifts (δ) are relative to TMS (δ = 0.00) as internal standard and expressed in parts per million. The number of protons (*n*) for a given resonance is indicated as *n* H. Standard abbreviations are used to denote spin multiplicities. Coupling constants (*J*) are given in hertz. Elemental analyses were recorded using a Thermo Finnigan FLASH EA 1112CHN analyzer. All compounds gave C, H and N analysis within ± 0.4% of the theoretical values. Column chromatography was performed using a mixture of PE and EtOAc on silica gel (100–200 mesh, Sisco Research Laboratories, India). Analytical TLC was performed on precoated plastic sheets of silica gel G/UV-254 of 0.2 mm thickness (Macherey-Nagel, Germany) using analytical grade solvents and visualized with I_2 spray (10% w/w I_2 in silica gel), UV light (λ = 254 and 365 nm) and alkaline $KMnO_4$ solution.

Dimerization of 1a; Typical Procedure

In a screw cap vial at 25 °C, under an argon atmosphere was charged $Au_2(BIPHEP)(NTf_2)_2$ (37.2 mg (2.5 mol%). To this was added a freshly prepared solution of 2-ethynylaniline (**1a**; 117 mg, 1 mmol) in anhydrous 1,2-dichloroethane (1 mL) and stirred at 25 °C for 6 h. Then the reaction mixture was quenched with H_2O (5 mL) and extracted with CH_2Cl_2 (3 × 5 mL). The combined organic extracts were dried (Na_2SO_4), filtered, and concentrated under reduced pressure. The crude material was purified by column chromatography (silica gel) using cyclohexane–EtOAc eluent system to afford the desired dimerization product **2a**.

2-(4-Methylquinolin-2-yl)phenylamine (2a)

Yield: 220 mg (94%); yellow solid; mp 78–80 °C.

IR (KBr): 3454, 3330, 1612, 1447, 1242, 1157, 947, 751 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 8.04 (d, *J* = 8.4 Hz, 1 H), 7.96 (d, *J* = 8.4 Hz, 1 H), 7.66–7.69 (m, 3 H), 7.52 (t, *J* = 6.9 Hz, 1 H), 7.19 (t, *J* = 8.1 Hz, 1 H), 6.80 (q, *J* = 12.2 Hz, 2 H), 6.15 (br s, 2 H), 2.74 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 159.0, 147.4, 146.7, 144.8, 130.2, 129.9, 129.5, 129.4, 126.5, 126.0, 123.7, 121.9, 121.2, 117.5, 117.3, 19.1.

MS (ESI): *m*/*z* = 235 [M + H^+].

Anal. Calcd for $C_{16}H_{14}N_2$: C, 82.02; H, 6.02; N, 11.96. Found: C, 81.91; H, 6.05; N, 12.04.

2-(4,6-Dimethylquinolin-2-yl)-4-methylphenylamine (2b)

Yield: 234 mg (89%); yellow solid; mp 146–148 °C.

IR (KBr): 3425, 3327, 1604, 1423, 1216, 1119, 899, 726 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.92 (d, *J* = 8.0 Hz, 1 H), 7.61 (s, 1 H), 7.71 (s, 1 H), 7.50 (dd, J_1 = 8.0 Hz, J_2 = 1.5 Hz, 1 H), 7.00 (d, *J* = 8.1 Hz, 1 H), 7.48 (s, 1 H), 6.71 (d, *J* = 8.1 Hz, 1 H), 5.89 (br s, 2 H), 2.69 (s, 3 H), 2.54 (s, 3 H), 2.32 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 158.2, 145.3, 144.7, 144.0, 135.6, 131.3, 130.7, 130.0, 129.1, 126.5, 126.4, 122.6, 122.0, 121.2, 117.4, 21.8, 20.7, 19.1.

MS (ESI): *m*/*z* = 263 [M + H^+].

Anal. Calcd for $C_{18}H_{18}N_2$: C, 82.41; H, 6.92; N, 10.68. Found: C, 82.50; H, 6.89; N, 10.62.

2-(6-Fluoro-4-methyl-2-quinolinyl)-4-fluorophenylamine (2c)

Yield: 173 mg (64%); yellow solid; mp 117–119 °C.

IR (KBr): 3466, 3347, 1453, 1286, 909, 786 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 8.00 (dd, J_1 = 9.0 Hz, J_2 = 4.0 Hz, 1 H), 7.56–7.58 (m, 2 H), 7.45 (td, J_1 = 9.0 Hz, J_2 = 2.6 Hz, 1 H), 7.35 (dd, J_1 = 9.0 Hz, J_2 = 2.6 Hz, 1 H), 6.93 (td, J_1 = 9.0 Hz, J_2 = 2.6 Hz, 1 H), 6.84 (dd, J_1 = 9.0 Hz, J_2 = 4.0 Hz, 1 H), 5.88 (br s, 2 H), 2.71 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 160.4 (d, $J_{C,F}$ = 245.0 Hz), 157.1, 156.4, 154.6, 144.5 (d, $J_{C,F}$ = 5.9 Hz), 143.5 (d, $J_{C,F}$ = 32.4 Hz), 131.7 (d, $J_{C,F}$ = 9.5 Hz), 127.3 (d, $J_{C,F}$ = 9.7 Hz), 122.0 (d, $J_{C,F}$ = 6.8 Hz), 119.3 (d, $J_{C,F}$ = 25.0 Hz), 121.5, 118.1 (d, *J* = 6.7 Hz), 117.0 (d, $J_{C,F}$ = 22.0 Hz), 115.3 (d, $J_{C,F}$ = 23.9 Hz), 107.3 (d, $J_{C,F}$ = 22.0 Hz), 19.2.

MS (ESI): *m*/*z* = 271 [M + H^+].

Anal. Calcd for $C_{16}H_{12}F_2N_2$: C, 71.10; H, 4.48; N, 10.36. Found: C, 70.97; H, 4.52; N, 10.41.

2-(4-Methyl-6-nitroquinolin-2-yl)-4-nitrophenylamine (2d)

Yield: 227 mg (70%); yellow solid; mp 244–246 °C.

IR (KBr): 3481, 3367, 1556, 1444, 1354, 1247, 899, 701 cm^{-1}.

^1H NMR (500 MHz, DMSO-d_6): δ = 9.06 (d, *J* = 2.6 Hz, 1 H), 8.85 (s, 1 H), 8.52 (dd, J_1 = 9.2 Hz, J_2 = 2.5 Hz, 1 H), 8.29 (d, *J* = 9.1 Hz, 1 H), 8.09 (dd, J_1 = 9.1 Hz, J_2 = 2.5 Hz, 1 H), 6.94 (d, *J* = 2.6 Hz, 1 H), 6.84 (d, *J* = 8.9 Hz, 1 H), 6.51 (br s, 2 H), 2.58 (s, 3 H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 154.8, 153.0, 148.9, 145.5, 114.8, 135.5, 131.2, 130.8, 127.1, 126.7, 125.8, 122.2, 121.4, 119.6, 113.3, 15.0.

MS (ESI): *m*/*z* = 325 [M + H^+].

Anal. Calcd for $C_{16}H_{12}N_4O_4$: C, 59.26; H, 3.73; N, 17.28. Found: 59.35; H, 3.71; N, 17.22.

2-(6-Chloro-4-methyl-2-quinolinyl)-4-chlorophenylamine (2e)

Yield: 247 mg (81%); yellow solid; mp 147–149 °C.

IR (KBr): 3413, 3351, 1438, 1268, 865, 766 cm^{-1}.

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^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.99 (s, 1 H), 7.93 (s, 1 H), 7.63–7.69 (m, 2 H), 7.13 (d, *J* = 8.4 Hz, 1 H), 6.72 (d, *J* = 8.4 Hz, 1 H), 6.57 (d, *J* = 9.2 Hz, 1 H), 6.16 (br s, 2 H), 2.68 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 157.8, 148.8, 146.1, 144.4, 134.2, 132.0, 129.0, 127.4, 125.4, 122.9, 121.9, 121.5, 120.1, 118.6, 102.4, 19.0.

MS (ESI): *m*/*z* = 303 [M + H$^+$], 305 [M + 2 + H$^+$], 307 [M + 4 + H$^+$].

Anal. Calcd for $C_{16}H_{12}Cl_2N_2$: C, 63.38; H, 3.99; N, 9.24. Found: C, 63.52; H, 3.92; N, 9.15.

2-(2-Amino-5-cyanophenyl)-4-methylquinoline-6-carbonitrile (2f)

Yield: 225 mg (79%); yellow solid; mp 296–298 °C.

IR (KBr): 3487, 3356, 2266, 1403, 1277, 857, 772 cm^{-1}.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 8.67 (s, 1 H), 8.38 (s, 1 H), 8.20–8.24 (m, 2 H), 8.04 (d, *J* = 9.0 Hz, 1 H), 7.50 (d, *J* = 9.0 Hz, 1 H), 6.94 (d, *J* = 9.2 Hz, 1 H), 6.02 (br s, 2 H), 2.77 (s, 3 H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 159.0, 152.4, 146.8, 146.0, 134.5, 1332.2, 130.6, 130.2, 129.9, 125.3, 121.0, 119.9, 118.6, 117.0, 116.9, 108.1, 95.8, 17.8.

MS (ESI): *m*/*z* = 285 [M + H$^+$].

Anal. Calcd for $C_{18}H_{12}N_4$: C, 76.04; H, 4.25; N, 19.71. Found: C, 75.95; H, 4.29; N, 19.76.

2-(7-Methoxy-4-methyl-2-quinolinyl)-5-methoxyphenylamine (2g)

Yield: 256 mg (87%); yellow solid; mp 124–126 °C.

IR (KBr): 3456, 3367, 1403, 1216, 809, 716 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.85 (d, *J* = 9.2 Hz, 1 H), 7.62 (d, *J* = 9.2 Hz, 1 H), 7.47 (s, 1 H), 7.34 (d, *J* = 2.4 Hz, 1 H), 7.14 (dd, J_1 = 9.2 Hz, J_2 = 2.5 Hz, 1 H), 6.38 (dd, J_1 = 9.2 Hz, J_2 = 2.5 Hz, 1 H), 6.33 (br s, 2 H), 6.30 (d, *J* = 2.6 Hz, 1 H), 3.95 (s, 3 H), 3.82 (s, 3 H), 2.68 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 161.5, 160.2, 159.2, 149.2, 148.5, 144.3, 131.1, 124.6, 121.2, 118.8, 118.0, 115.2, 107.5, 104.2, 101.3, 55.5, 55.2, 19.0.

MS (ESI): *m*/*z* = 295 [M + H$^+$].

Anal. Calcd for $C_{18}H_{18}N_2O_2$: C, 73.45; H, 6.16; N, 9.52. Found: C, 73.52; H, 6.14; N, 9.49.

2-(4,6,7-Trimethyl-2-quinolinyl)-4,5-dimethylphenylamine (2h)

Yield: 275 mg (95%); yellow solid; mp 184–186 °C.

IR (KBr): 3466, 3327, 1423, 1256, 899, 766 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.78 (s, 1 H), 7.66 (s, 1 H), 7.55 (s, 1 H), 7.43 (s, 1 H), 6.61 (s, 1 H), 5.97 (br s, 2 H), 2.69 (s, 3 H), 2.46 (s, 3 H), 2.44 (s, 3 H), 2.24 (s, 3 H), 2.22 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 158.1, 145.9, 143.3, 140.1, 139.0, 138.6, 135.3, 130.3, 128.8, 125.3, 124.8, 123.0, 120.1, 119.9, 118.6, 20.3, 20.2, 19.7, 19.1, 19.0.

MS (ESI): *m*/*z* = 291 [M$^+$ + H$^+$].

Anal. Calcd for $C_{20}H_{22}N_2$: C, 82.72; H, 7.64; N, 9.65. Found: C, 82.85; H, 7.59; N, 9.58.

4-Bromo-2-(6-bromo-8-chloro-4-methylquinolin-2-yl)-6-chlorophenylamine (2i)

Yield: 338 mg (73%); yellow oil.

IR (thin film): 3512, 3487, 1602, 1287, 950, 802 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.99 (s, 1 H), 7.79 (d, *J* = 2.3 Hz, 1 H), 7.70 (s, 1 H), 7.44 (d, *J* = 2.3 Hz, 1 H), 6.79 (br s, 2 H), 7.90 (d, *J* = 1.5 Hz, 1 H), 2.69 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 163.0, 156.8, 152.3, 143.8, 138.0, 132.8, 132.5, 131.4, 130.1, 128.2, 125.2, 121.4, 121.1, 119.7, 110.7, 26.8.

MS (ESI): *m*/*z* = 461 [M + H$^+$], 463 [M + 2 + H$^+$], 465 [M + 4 + H$^+$].

Anal. Calcd for $C_{16}H_{10}Br_2Cl_2N_2$: C, 41.69; H, 2.19; N, 6.08. Found: C, 41.85; H, 2.15; N, 6.00.

2,4-Dimethyl-6-(6,8-dimethyl-4-methyl-2-quinolinyl)phenylamine (2j)

Yield: 278 mg (96%); yellow oil.

IR (thin film): 3447, 3298, 1511, 1205, 915, 789 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.72 (s, 1 H), 7.63 (s, 1 H), 7.51 (s, 1 H), 7.43 (s, 1 H), 7.01 (s, 1 H), 6.45 (br s, 2 H), 2.81 (s, 3 H), 2.74 (s, 3 H), 2.56 (s, 3 H), 2.37 (s, 3 H), 2.29 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 157.0, 144.0, 143.4, 136.4, 135.1, 132.1, 131.0, 127.9, 124.3, 124.0, 121.0, 120.7, 119.9, 118.0, 21.9, 21.5, 19.5, 18.8, 18.0.

MS (ESI): *m*/*z* = 291 [M + H$^+$].

Anal. Calcd for $C_{20}H_{22}N_2$: C, 82.72; H, 7.64; N, 9.65. Found: C, 82.87; H, 7.59; N, 9.55.

2-Chloro-6-(6-chloro-4,8-dimethylquinolin-2-yl)-4-methylphenylamine (2k)

Yield: 256 mg (77%); yellow oil.

IR (thin film): 3361, 3300, 1600, 1147, 841 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.13 (s, 1 H), 7.81 (s, 1 H), 7.66 (s, 1 H), 7.63 (s, 1 H), 6.97 (s, 1 H), 5.10 (br s, 2 H), 2.57 (s, 3 H), 2.52 (s, 3 H), 2.42 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 151.0, 143.5, 141.1, 137.2, 135.0, 131.9, 130.4, 128.3, 127.5, 125.4, 124.5, 123.3, 117.7, 108.4, 100.0, 21.3, 19.9, 19.4.

MS (ESI): *m*/*z* = 331 [M + H$^+$], 333 [M + 2 + H$^+$], 335 [M + 4 + H$^+$].

Anal. Calcd for $C_{18}H_{16}Cl_2N_2$: C, 65.27; H, 4.87; N, 8.46. Found: C, 65.48; H, 4.95; N, 8.39.

2,4-Dibromo-6-(6,8-dibromo-4-methyl-2-quinolinyl)phenylamine (2l)

Yield: 415 mg (75%); yellow solid; mp 186–188 °C.

IR (KBr): 3751, 3413, 2956, 2430, 1457, 766 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.71 (s, 1 H), 8.19 (d, *J* = 2.3 Hz, 1 H), 8.14 (d, *J* = 2.3 Hz, 1 H), 7.65 (d, *J* = 2.2 Hz, 1 H), 7.10 (d, *J* = 2.3 Hz, 1 H), 4.12 (br s, 2 H), 2.51 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 162.8, 152.1, 143.2, 141.6, 136.0, 134.9, 132.1, 131.4, 129.9, 126.7, 126.6, 124.7, 120.7, 110.1, 109.2, 26.9.

MS (ESI) *m*/*z* = 551 [M + H$^+$], 553 [M + 2 + H$^+$], 555 [M + 4 + H$^+$].

Anal. Calcd for $C_{16}H_{10}Br_4N_2$: C, 34.95; H, 1.83; N, 5.09. Found: C, 35.07; H, 1.78; N, 5.00.

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2-Methoxy-6-(8-methoxy-4-methyl-6-nitroquinolin-2-yl)-4-nitrophenylamine (2m)

Yield: 230 mg (60%); brown solid; mp 264–266 °C.

IR (KBr): 3369, 2924, 1615, 1501, 1323, 1093, 740 cm^{-1}.

^1H NMR (500 MHz, DMSO-d_6): δ = 8.71 (s, 1 H), 8.55 (s, 1 H), 7.80 (s, 1 H), 7.67 (s, 2 H), 6.12 (br s, 2 H), 4.07 (s, 3 H), 3.93 (s, 3 H), 2.47 (s, 3 H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 157.1, 153.7, 146.2, 145.9, 145.5, 144.2, 141.9, 135.9, 129.1, 121.0, 119.2, 113.4, 105.5, 101.6, 100.0, 60.3, 57.0, 21.2.

MS (ESI): m/z = 385 [M + H^+].

Anal. Calcd for $C_{18}H_{16}N_4O_6$: C, 56.25; H, 4.20; N, 14.58. Found: C, 56.45; H, 4.12; N, 14.49.

Methyl 2-(2-Amino-3-methoxy-5-methoxycarbonylphenyl)-8-methoxy-4-methylquinoline-6-carboxylate (2n)

Yield: 312 mg (76%); colorless solid; mp 156–158 °C.

IR (KBr): 3394, 2955, 1677, 1081, 756 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 8.14 (s, 1 H), 8.06 (s, 1 H), 7.41 (s, 1 H), 7.31 (s, 1 H), 7.21 (d, J = 3.05 Hz, 1 H), 6.58 (br s, 2 H), 3.96 (s, 3 H), 3.91 (s, 3 H), 3.89 (s, 3 H), 3.88 (s, 3 H), 2.60 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 168.4, 166.9, 150.1, 146.6, 145.7, 145.3, 131.2, 128.4, 127.1, 125.0, 122.5, 117.3, 116.1, 115.5, 112.9, 104.3, 102.4, 55.9, 55.5, 51.9, 29.7, 28.1.

MS (ESI): m/z = 411 [M + H^+].

Anal. Calcd for $C_{22}H_{22}N_2O_6$: C, 64.38; H, 5.40; N, 6.83. Found: C, 64.52; H, 5.35; N, 6.77.

2-Methoxy-6-(8-methoxy-4-methyl-6-tritylquinolin-2-yl)-4-tritylaniline (2o)

Yield: 498 mg (64%); colorless solid; mp 144–146 °C.

IR (KBr): 3375, 2989, 1601, 1165, 920, 781 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.90 (s, 1 H), 7.78–7.67 (m, 7 H), 7.55 (s, 1 H), 7.52–7.35 (m, 12 H), 7.31–7.24 (m, 6 H), 7.20–7.12 (m, 6 H), 7.01 (s, 1 H), 6.99 (s, 1 H), 6.96 (s, 1 H), 5.99 (br s, 2 H), 3.89 (s, 3 H), 3.85 (s, 3 H), 2.64 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 155.5, 149.6, 148.6, 144.4, 138.1, 136.4, 135.8, 132.9, 130.3, 129.7, 126.6, 125.8, 122.9, 122.5, 121.8, 121.5, 120.8, 120.1, 117.1, 111.9, 111.1, 102.6, 64.9, 64.3, 55.5, 54.9, 19.8.

MS (ESI): m/z = 779 [M + H^+].

Anal. Calcd for $C_{56}H_{46}N_2O_2$: C, 86.34; H, 5.95; N, 3.60. Found: C, 85.99; H, 6.00; N, 3.66.

Methyl 2-[2-Amino-5-(methoxycarbonyl)-3-methylphenyl]-4,8-dimethylquinoline-6-carboxylate (2p)

Yield: 280 mg (74%); yellow solid; mp 174–176 °C.

IR (KBr): 3401, 2988, 1599, 1175, 928, 791 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 8.13 (s, 1 H), 8.01 (s, 1 H), 7.79 (s, 1 H), 7.44 (s, 1 H), 7.05 (s, 1 H), 3.95 (s, 3 H), 3.89 (s, 3 H), 2.66 (s, 3 H), 2.25 (s, 3 H), 2.20 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 168.8, 167.9, 156.8, 156.5, 150.1, 148.2, 137.9, 130.0, 127.1, 125.7, 122.8, 121.6, 120.5, 120.3, 117.7, 53.2, 51.4, 20.1, 19.1, 17.7.

MS (ESI): m/z = 379 [M + H^+].

Anal. Calcd for $C_{22}H_{22}N_2O_4$: C, 69.83; H, 5.86; N, 7.40. Found: C, 70.09; H, 5.79; N, 7.32.

3,5-Dimethyl-2-(4,5,7-trimethylquinolin-2-yl)aniline (2q)

Yield: 261 mg (90%); pale yellow solid; mp 114–116 °C.

IR (KBr): 3436, 3277, 1513, 1207, 918, 799 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.62 (s, 1 H), 7.41 (s, 1 H), 6.97 (s, 1 H), 6.53 (s, 1 H), 6.07 (br s, 2 H), 2.59 (s, 3 H), 2.54 (s, 3 H), 2.37, (s, 3 H), 2.34 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 158.2, 145.7, 143.0, 140.5, 139.2, 138.1, 135.1, 130.1, 128.8, 125.0, 124.4, 123.0, 120.0, 119.9, 118.5, 20.2, 20.1, 19.7, 19.0, 18.9.

MS (ESI): m/z = 291 [M + H^+].

Anal. Calcd for $C_{20}H_{22}N_2$: C, 82.72; H, 7.64; N, 9.65. Found: C, 83.01; H, 7.56; N, 9.45.

2-(4,5-Dimethylquinolin-2-yl)-3-methylaniline (2r)

Yield: 225 mg (86%); pale yellow solid; mp 139–141 °C.

IR (KBr): 3319, 3021, 1525, 1199, 904, 754 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.88 (d, J = 8.1 Hz, 1 H), 7.65 (t, J = 7.6 Hz, 1 H), 7.50 (d, J = 7.6 Hz, 1 H), 7.22 (t, J = 8.1 Hz, 1 H), 7.01 (s, 1 H), 6.78 (d, J = 7.6 Hz, 1 H), 6.64 (d, J = 8.1 Hz, 1 H), 6.07 (br s, 2 H), 2.63 (s, 3 H), 2.55 (s, 3 H), 2.50 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 158.5, 145.5, 144.3, 144.5, 135.1, 131.9, 130.0, 130.1, 129.2, 126.5, 126.3, 122.5, 122.0, 121.2, 117.4, 21.7, 20.3, 18.9.

MS (ESI): m/z = 263 [M + H^+].

Anal. Calcd for $C_{18}H_{18}N_2$: C, 82.41; H, 6.92; N, 10.68. Found: C, 82.25; H, 6.96; N, 10.80.

3-(4,6-Dimethyl-1,8-naphthyridin-2-yl)-5-methylpyridin-2-amine (2s)

Yield: 137 mg (52%); yellow solid; mp 227–229 °C.

IR (KBr): 3444, 2975, 1311, 947, 729 cm^{-1}.

^1H NMR (500 MHz, DMSO-d_6): δ = 8.99 (s, 1 H), 8.41 (s, 1 H), 7.80 (s, 1 H), 7.34 (s, 1 H), 7.01 (s, 1 H), 4.62 (br s, 2 H), 2.42 (s, 3 H), 2.37 (s, 3 H), 2.35 (s, 3 H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 153.6, 150.8, 150.3, 149.9, 147.2, 146.5, 135.0, 134.3, 133.8, 123.9, 121.2, 115.1, 112.3, 21.1, 18.9, 18.7.

MS (ESI): m/z = 265 [M + H^+].

Anal. Calcd for $C_{16}H_{16}N_4$: C, 72.70; H, 6.10; N, 21.20. Found: C, 72.97; H, 6.13; N, 20.90.

3-(4-Methyl-6-nitro[1,8]naphthyridin-2-yl)-5-nitropyridin-2-ylamine (2t)

Yield: 134 mg (41%); yellow solid; mp 251–253 °C.

IR (KBr): 3450, 2961, 1599, 1400, 1218, 950, 715 cm^{-1}.

^1H NMR (500 MHz, DMSO-d_6): δ = 9.04 (s, 1 H), 8.83 (s, 1 H), 7.70 (s, 1 H), 7.52 (s, 1 H), 6.70 (s, 1 H), 4.57 (br s, 2 H), 2.46 (s, 3 H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 163.3, 147.0, 139.3, 135.8, 134.5, 132.6, 132.0, 131.9, 129.3, 129.2, 125.1, 103.2, 100.5, 20.6.

MS (ESI): m/z = 327 [M + H^+].

Anal. Calcd for $C_{14}H_{10}N_6O_4$: C, 51.54; H, 3.09; N, 25.76. Found: C, 51.75; H, 3.00; N, 25.68.

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Competitive Dimerization of 1a with Phenylacetylene (4a); Typical Procedure

In a screw cap vial at 25 °C, under an argon atmosphere was charged $Au_2(BIPHEP)(NTf_2)_2$ (37.2 mg, 2.5 mol%). To this was added a freshly mixed solution of 2-ethynylaniline (**1a**; 117 mg, 1 mmol), phenylacetylene (**4a**; 102 mg, 1 mmol) in anhydrous 1,2-dichloroethane (1 mL) and stirred at 25 °C for 6 h. Then the reaction mixture was quenched with H_2O (5 mL) and extracted with CH_2Cl_2 (3 × 5 mL). The combined organic extracts were dried (Na_2SO_4), filtered, and concentrated under reduced pressure. The crude material was purified by column chromatography (silica gel) using cyclohexane–EtOAc eluent system to separate the dimerization product **2a** and the addition product **5a**.

4-Methyl-2-phenylquinoline (5a)

Yield: 116 mg (53%); yellow paste.

IR (KBr): 3040, 1590, 1544, 1565, 1444, 1406, 1345, 765, 728, 699 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 8.22–8.16 (m, 3 H), 8.00 (d, *J* = 8.4 Hz, 1 H), 7.75–7.70 (m, 2 H), 7.57–7.44 (m, 4 H), 2.78 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 157.0, 148.2, 144.8, 139.9, 130.3, 129.3, 129.2, 128.8, 127.5, 127.3, 126.0, 123.6, 119.6, 18.8.

MS (ESI): *m*/*z* = 220 [M + H^+].

4-Methyl-2-(*p*-tolyl)quinoline (5b)

Yield: 151 mg (65%); yellow paste.

IR (KBr): 3055, 2920, 1587, 1571, 1485, 1344, 814, 750 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 8.16 (d, *J* = 8.3 Hz, 1 H), 8.06 (d, *J* = 7.6 Hz, 2 H), 7.99 (d, *J* = 8.2 Hz, 1 H), 7.71–7.69 (m, 2 H), 7.55–7.51 (m, 1 H), 7.33 (d, *J* = 7.6 Hz, 2 H), 2.76 (s, 3 H), 2.44 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 157.0, 148.3, 144.6, 139.2, 137.1, 130.3, 129.5, 129.2, 127.4, 127.2, 125.8, 123.6, 119.6, 21.3, 18.9.

MS (ESI): *m*/*z* = 234 [M + H^+].

2-(4-Methoxyphenyl)-4-methylquinoline (5c)

Yield: 159 mg (64%); pale yellow solid; mp 59–61 °C.

IR (KBr): 3060, 1589, 1488, 1431, 1355, 1200, 1044, 771, 705 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 8.13 (d, *J* = 8.5 Hz, 3 H), 7.98 (d, *J* = 8.2 Hz, 1 H), 7.72–7.68 (m, 2 H), 7.52 (t, *J* = 7.4 Hz, 1 H), 7.04 (d, *J* = 8.6 Hz, 2 H), 3.89 (s, 3 H), 2.76 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 160.7, 156.7, 148.2, 144.6, 132.4, 130.1, 129.3, 128.9, 127.0, 125.7, 123.6, 119.3, 114.2, 55.4, 19.0.

MS (ESI): *m*/*z* = 250 [M + H^+].

2-(4-Chlorophenyl)-4-methylquinoline (5d)

Yield: 74 mg (29%); colorless solid; mp 93–95 °C..

IR (KBr): 3061, 1589, 1545, 1073, 878, 793, 773, 711 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 8.17–8.10 (m, 3 H), 8.00 (d, *J* = 8.2 Hz, 1 H), 7.75–7.68 (m, 2 H), 7.57–7.48 (m, 3 H), 2.77 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 155.7, 148.2, 145.0, 138.2, 135.4, 130.3, 129.5, 128.9, 128.8, 127.3, 126.2, 123.6, 119.3, 18.9.

MS (ESI): *m*/*z* = 254 [M + H^+], 256 [M + 2 + H^+].

2-(2-Chlorophenyl)-4-methylquinoline (5e)

Yield: 66 mg (26%); colorless solid; mp 112–114 °C.

IR (KBr): 3029, 1575, 1522, 1050, 800, 706 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 8.18 (d, *J* = 8.4 Hz, 1 H), 8.05 (d, *J* = 8.2 Hz, 1 H), 7.74–7.50 (m, 5 H), 7.42–7.35 (m, 2 H), 2.77 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 157.2, 148.0, 143.9, 139.9, 132.4, 131.7, 130.3, 130.1, 129.7, 129.3, 127.3, 127.1, 126.5, 123.7, 123.4, 18.8.

MS (ESI): *m*/*z* = 254 [M + H^+], 256 [M + 2 + H^+].

4-Methyl-2-(*m*-tolyl)quinoline (5f)

Yield: 135 mg (58%); yellow liquid.

IR (KBr): 3059, 2922, 1580, 1573, 1484, 804, 747 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 8.18 (d, *J* = 8.3 Hz, 1 H), 8.01–7.99 (m, 2 H), 7.91 (d, *J* = 7.5 Hz, 1 H), 7.74–7.71 (m, 2 H), 7.54 (t, *J* = 7.4 Hz, 1 H), 7.41 (t, *J* = 7.5 Hz, 1 H), 7.28–7.26 (m, 1 H), 2.77 (s, 3 H), 2.48 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 157.3, 148.3, 144.7, 139.9, 138.4, 130.4, 130.0, 129.3, 128.7, 128.3, 127.3, 126.0, 124.7, 123.6, 119.9, 21.6, 18.9.

MS (ESI): *m*/*z* = 234 [M + H^+].

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Supporting Information

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