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Gold(III)-Catalyzed Site-Selective and Divergent Synthesis of 2-Aminopyrroles and Quinoline-Based Polyazaheterocycles

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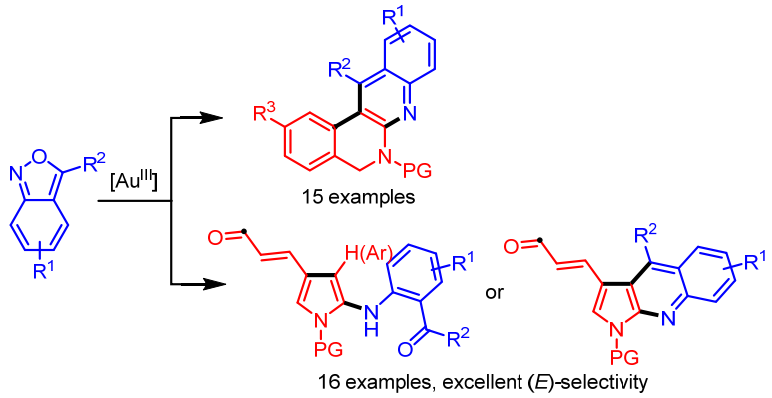
Abstract: We herein describe a facile, site-selective and divergent approach to construct 2-aminopyrroles and quinoline-fused polyazaheterocycles enabled by a simple gold(III) catalyst from ynamides and anthranils under mild reaction conditions. This one-pot strategy uses readily available starting materials, proceeds in a highly step- and atom-economical manner, with broad substrate scope and scale-up potential. The key element for success in this tandem reaction is a catalyst-directed preferred quenching of the *in-situ* generated gold carbene intermediates by a nucleophilic benzyl/2-furylmethyl moiety on the ynamides as an alternative to the known C–H annulation leading to indoles.



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The efficient and rapid synthesis of aza-heterocycles is of high significance for synthetic and medicinal chemistry[1] and material science.[2] 2-Aminopyrroles[3] as well as quinoline-fused poly-aza-heterocycles, such as pyrrolo[2,3-*b*]quinoline[4] and dihydrodibenzo[*b*,*f*][1,8]naphthyridine derivatives,[5,6f] are fundamental motifs in numerous pharmaceuticals, natural products, and organic functional materials. Several synthetic routes towards these quinoline-fused polyazaheterocycles have been developed.[6] However, most methods involve multiple-step syntheses from the relevant quinoline precursors, and suffer from low functional group tolerance.[6] More important, the installation of a propenal side chain to the parent pyrrole ring is also a challenge, making it difficult to construct the pyrrolo[2,3-*b*]quinolines with such a valuable grip.[6a-d] To this end, the development of a novel, general, and environmentally benign method towards these polyazaheterocycles in a selective and divergent fashion from easily accessible starting materials is still highly desired.

Recent rapid advances in gold carbene-promoted reactions have provided efficient and powerful strategies to access complex and diverse carbon- and azaheterocycles.[7] In this context, gold-catalyzed intra-/intermolecular nitrene transfers of azide moieties onto carbon-carbon triple bonds were used to prepare different azaheterocycles, including pyrroles,[8a-c] indoles,[8d-h] imidazoles,[8i] (iso)quinolines,[8j-m] and others.[8n-o] The azide moieties were generally introduced from sodium azide, a toxic and potentially explosive reagent. Intermolecular protocols to access α-imino gold carbene intermediates from non-toxic, safe and easily available nitrenoid precursors, are more practical and flexible. In line with this principle, various nitrenoid equivalents have been realized for intermolecular nitrene-transfer processes to ynamides, generating highly electrophilic gold carbene intermediates **A**.[9] Typically, a nucleophilic functionality tethered on the nitrene-transfer reagent traps the gold carbene, leading to formal [3+2] cycloadducts (Scheme 1, top);[9] or a new C–C double bond is formed via an 1,2-hydride shift if the α-hydrogens exist (middle).[9a,9o] The site-selective trapping by the R^1 substituent at the ynamide is more challenging, as the competing nucleophilic site Z can induce undesired side reactions. Recently, we disclosed a gold(I)-catalyzed synthesis of 7-acylindoles via the C–H^a annulation between alkynes and anthranils by exploiting the potential binucleophility of anthranils (Scheme 2, path a).[9n] We envisioned that the *in-situ* generated α-imino gold carbene species **A1** could be quenched by the C–H^b bond of *N*-benzyl ynamides as alternative to the C–H^a insertion known from the indole synthesis.[9n] Finally, the desired quinoline-embedded polyazaheterocycles would be formed via an nucleophilic addition of the enamin to the aldehyde and a subsequent elimination from intermediate **B1**. In this context a related approach using N-aryl ynamides as competing nucleophile, that was reported during the preparation of the manuscript must be mentioned here.[10]

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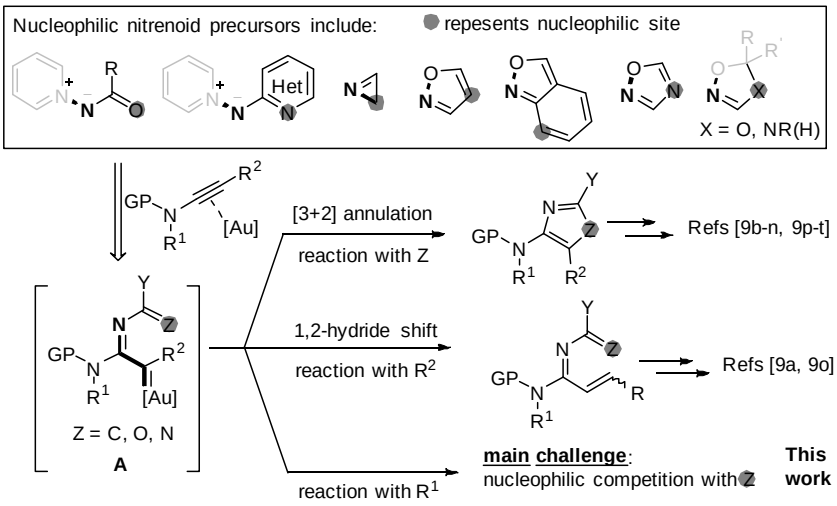
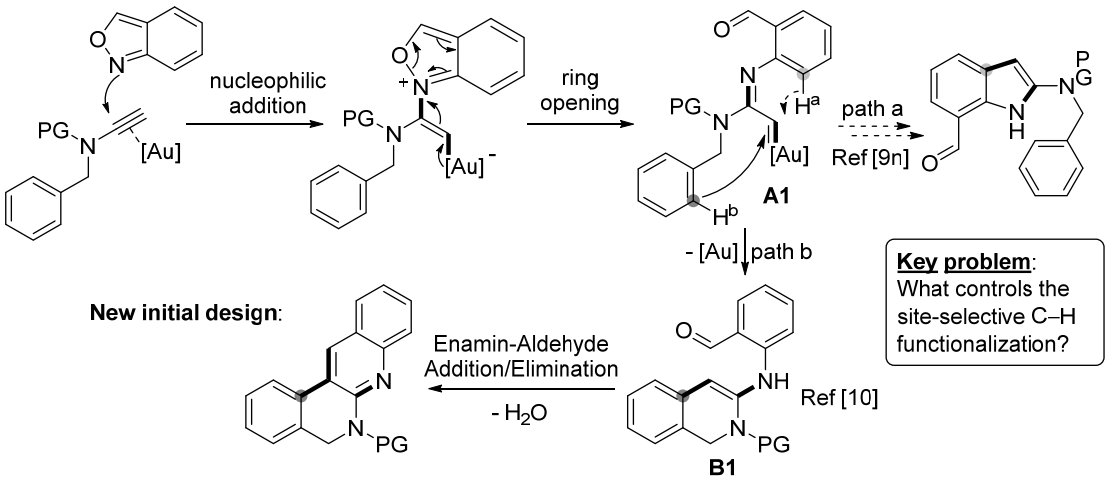


Scheme 1. Different site-selective reaction patterns of α-amino gold carbene intermediates.



Scheme 2. Site-selective C–H functionalization of the gold carbene intermediates. path a: our previous work; path b: present new initial design.

To evaluate the feasibility, *N*-benzyl ynamide **1a** and anthranil **2a** were initially chosen as the model substrates (Table 1). After screening, a "standard condition" (5 mol% $KAuBr_4$ in 1,2-DCE at –20 °C for 2 h; then heating to 40 °C for 10 h) was developed, which delivered product **3a** in 50% isolated yield accompanied by a small amount of the undesired indole product **4a** (Table 1, entry 1). Other tested gold(III) catalysts gave a similar ratio of **3a** and **4a** (entries 2–5). Switching to a cationic gold(I) complex favored the formation of indole product, the unactivated catalyst showed an unselective reaction (entries 6–7). The neutral ligand-free AuCl also worked in a selective manner, affording **3a** in 43% yield (about 5:1 **3a**:**4a**; entry 8). $PhCF_3$ as reaction medium did not improve the efficiency (entry 9). The control experiment in the absence of catalyst showed no conversion (entry 10).

Table 1: Representative examples from the optimization of the reaction conditions.[a]

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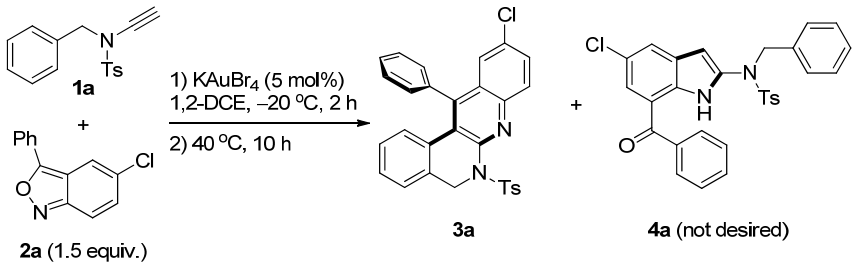

entry	deviation from "standard" conditions	yield of **3a**[b]	yield of **4a**[b]
1	None	54% (50%)	9
2	$NaAuBr_4$ as catalyst	50	14
3	$HAuBr_4$ as catalyst	49	15
4	$AuBr_3$ as catalyst	45	17
5	$PicAuCl_2$ as catalyst	47	14
6	$IPrAuCl/AgNTf_2$ as catalyst	27	37
7	IPrAuCl as catalyst	trace	Trace
8	10 mol % AuCl as catalyst	43	8
9	$PhCF_3$ instead of 1,2-DCE	48	12
10	no $KAuBr_4$	-	-

[a] "Standard" conditions: a solution of **1a** (0.1 mmol) in 1,2-DCE (0.5 mL) was added over 5 mins to a mixture of **2a** (0.15 mmol), $KAuBr_4$ (5 mol%) in 1,2-DCE (0.5 mL) at –20 °C and after 2 h the reaction mixture was heated to 40 °C for 10 h. [b] Measured by ^1H NMR with 1,3,5-trimethoxybenzene as the internal standard. Yield of isolated product given in parentheses.

Under the optimized conditions, a diverse set of *N*-benzyl ynamides with different anthranils were first tested (Table 2). Ynamides bearing different protecting groups (Ms, Ts, Bs, Ns, SO_2Ph) on nitrogen reacted quite well with anthranil **2a**, giving **3a–e** in satisfying yields. A scale-up (1 mmol) synthesis of **3e** provided a slightly lower yield. A tolyl group in **3f** delivered 58% yield. Various substituted anthranils were then examined. Besides a phenyl group (**3g**), methyl or hydrogen at the R^2 position afforded the desired products **3h** or **3i** in 48% and 62% yields, respectively. A less-polar carbon-carbon triple bond, that was also reactive in our previous work, remained intact.[9n] The obtained product **3j** emitted violet-blue fluorescence (Φ_F = 0.21), somewhat showcasing the importance of the compatibility with such a triple bond.Some other functional groups including chloride (**3k**), bromide (**3l**), ester (**3m**) and acetal (**3n**) were well tolerated, thus allowing further derivatization. If an aryl group was introduced at the C6 position of anthranils, **3o** was obtained in 60% yield. For the structural assignments of these products, single crystal X-ray structure analyses of **3b** and **3e** were conducted.[10]

Table 2: Substrate scope of *N*-benzyl ynamides and anthranils.[a]

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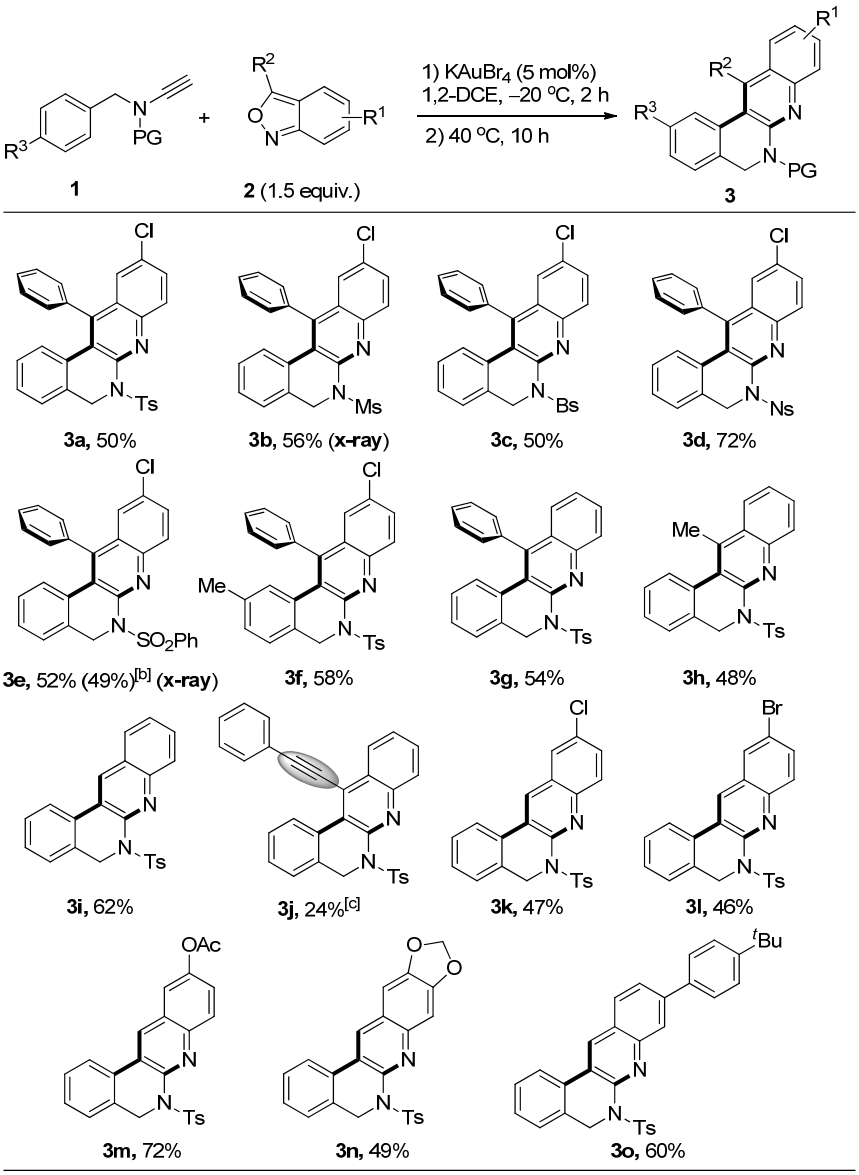

[a] Reaction conditions: a solution of **1** (0.12 mmol) in 1,2-DCE (1.2 mL) was added over 6 mins to a mixture of **2** (0.18 mmol), $KAuBr_4$ (5 mol%) in 1,2-DCE (1.2 mL) at –20 °C and after 2 h the reaction mixture was heated to 40 °C for 10 h; yield of isolated product. [b] 1 mmol scale. [c] heating to 80 °C for 10 h.

Electron-rich heteroaromatic systems tethered to the ynamide also can serve as an alternative nucleophilic site to trap the gold carbene intermediate were also tested. Under the above optimum condition, it was found that the treatment of *N*-furanylmethyl ynamide **5a** and anthranil **2a** proceeded well. However, the above expected tetracyclic *N*-heterocycles derived by C3–H insertion into the gold carbene were not obtained; instead pyrrole (*E*)-**6a** was isolated in 69% yield. Despite being thermodynamically less stable than its (*E*)-isomer, the isolation of (*Z*)-**6a** was also viable by just omitting the subsequent warming, which suggests the latter was likely to be generated first via a ring opening of furan by the regioselective attack of the C2-position to the gold carbene (Scheme 3). The primary product can be further transformed to the thermodynamically stable (*E*)-isomer **6a** or to tricyclic azaheterocycles (*E*)-**7a** via a Friedel-Crafts-type

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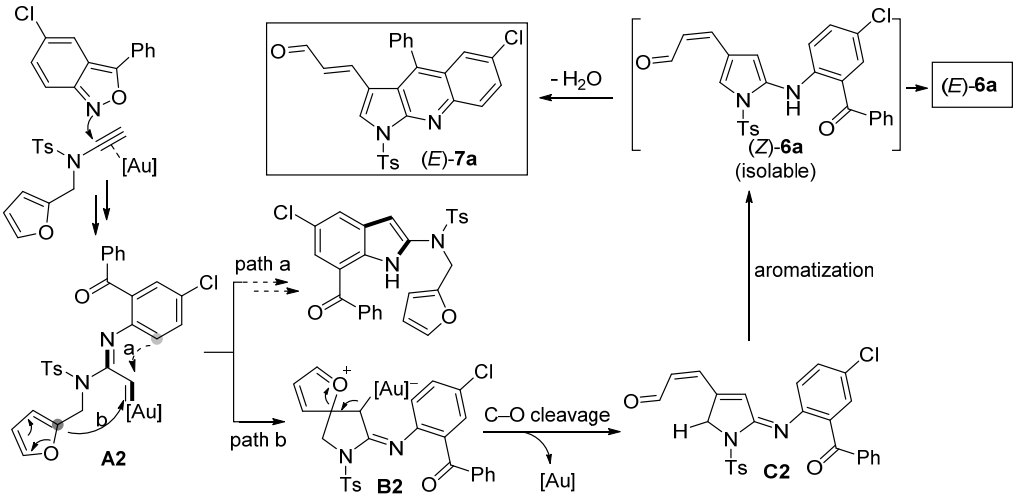
cyclization driven by heating or/and a Lewis acid.



Scheme 3. Proposed mechanism for the formation of 2-aminopyrroles and related products.

This synthetic strategy opens the route to 2-aminopyrroles **6** with a propenal side chain at C4 position. At this position such a versatile handle is not easy to be introduced, which distinguishes this method for pyrrole synthesis.[12] Besides, a myriad of potential derivatizations for the enal moiety could be anticipated, such as cycloaddition and some textbook transformations (oxidation, reduction and Michael addition).[13] With this in mind, various 2-aminopyrroles **6** were first investigated from anthranils and *N*-furanylmethyl ynamide **5a** at the temperature shown in Table 3. Aromatic (**6b**), aliphatic (**6c** and **6d**) and electronically neutral substituents (**6f**–**i**) as R^2 provided the desired products in moderate to good yields. Again, a carbon-carbon triple bond could be pre-installed on the anthranil substrate (**6e**). Other functional groups such as chloride (**6a**), methoxy (**6d** and **6f**), ester (**6g**), acetal (**6h**) were tolerated well. While internal *N*-benzyl ynamides were unsuccessful for the synthesis of **3**, the corresponding internal *N*-furanylmethyl derivative was converted into trisubstituted pyrrole **6j**. At a slightly high reaction temperature, some pyrrole-fused compounds **7** were also accessible in 35–59% yield in a one-pot process. A 45% yield of **7a** was isolated on an 1 mmol scale and its constitution was verified by single crystal X-ray diffraction.[11]

Table 3: Scope of the reaction between *N*-furanylmethyl ynamides and anthranils.[a]

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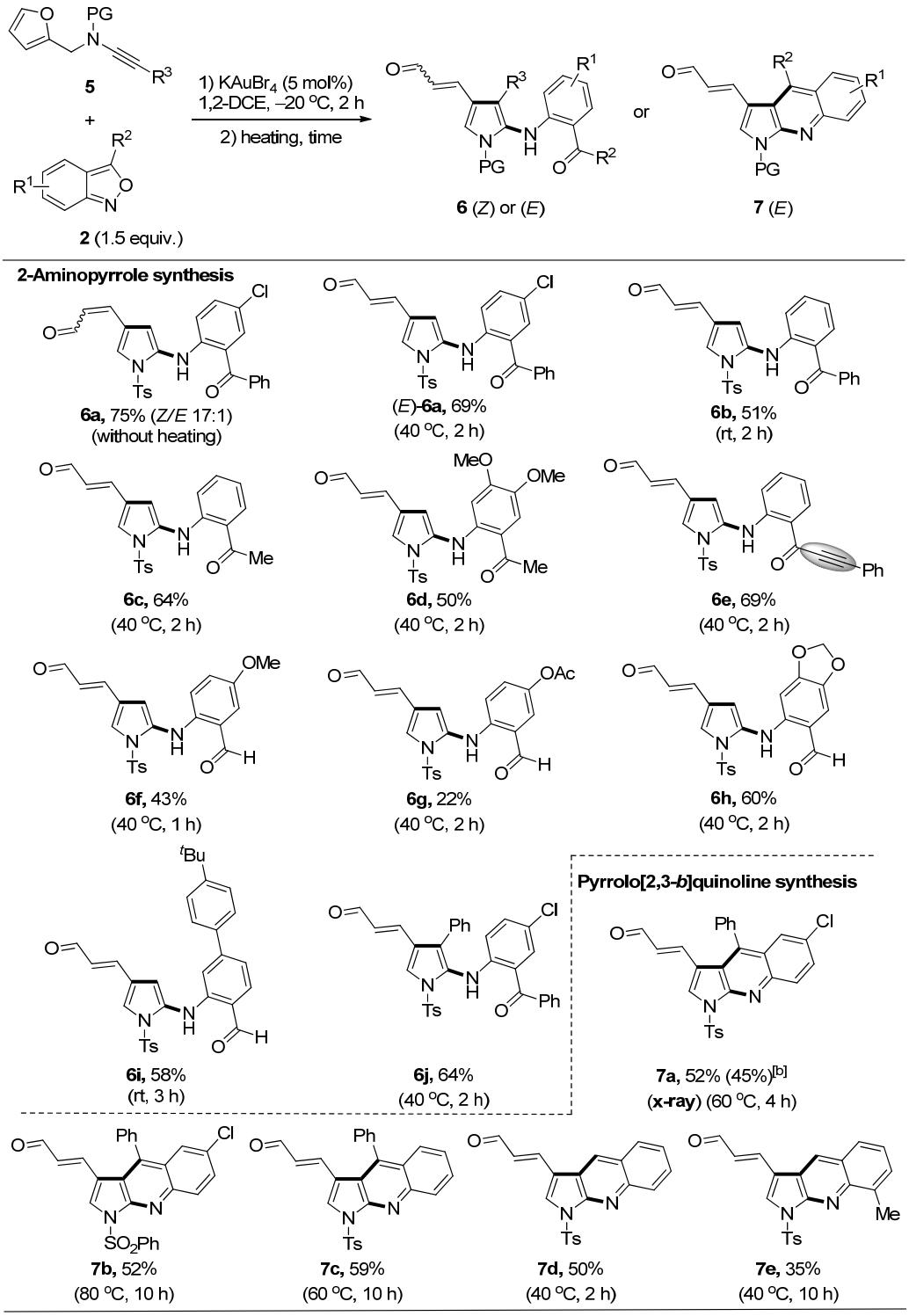

[a] Reaction conditions: a solution of **5** (0.12 mmol) in 1,2-DCE (1.2 mL) was added over 6 mins to a mixture of **2** (0.18 mmol), $KAuBr_4$ (5 mol%) in 1,2-DCE (1.2 mL) at –20 °C, and after 2 h the reaction mixture was heated for the given time; yield of isolated product. [b] 1 mmol scale.

In conclusion, an atom-economical, site-selective, divergent assembly of valuable and versatile 2-aminopyrroles and quinoline-fused polyazaheterocycles has been achieved. This protocol was enabled by a simple gold(III) catalyst leading to an preferable quenching of the gold carbene intermediate by a nucleophilic functionality on the ynamides, complementary to the C–H annulation known from the indole

synthesis. This will also open up a new window of opportunity for challenging intramolecular site-selective C–H functionalization. Unlike known synthetic methods, our strategy features a one-step operation, easily accessible starting materials, good functional-group tolerance, and scale-up potential accompanied by a broad substrate scope. Further studies on the application of anthranils for the synthesis of (π-extended) *N*-doped polycyclic aromatics are ongoing in our lab.

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Keywords: aminopyrroles • quinoline-embedded polyazaheterocycles • α-imino gold carbenes • anthranils • site-selective and divergent synthesis

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