Advanced Synthesis & Catalysis

## Accepted Article

**Title:** Gold-Catalyzed Aminoaromatizations of 1,2-Bis(alkynyl)benzenes with Anthranils to Yield 1-Amino-2-napthaldehyde Products

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**To be cited as:** *Adv. Synth. Catal.* 10.1002/adsc.202000591

**Link to VoR:** https://doi.org/10.1002/adsc.202000591

10.1002/adsc.202000591

FULL PAPER

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

# Gold-Catalyzed Aminoaromatizations of 1,2-Bis(alkynyl)benzenes with Anthranils to Yield 1-Amino-2-napthaldehyde Products

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

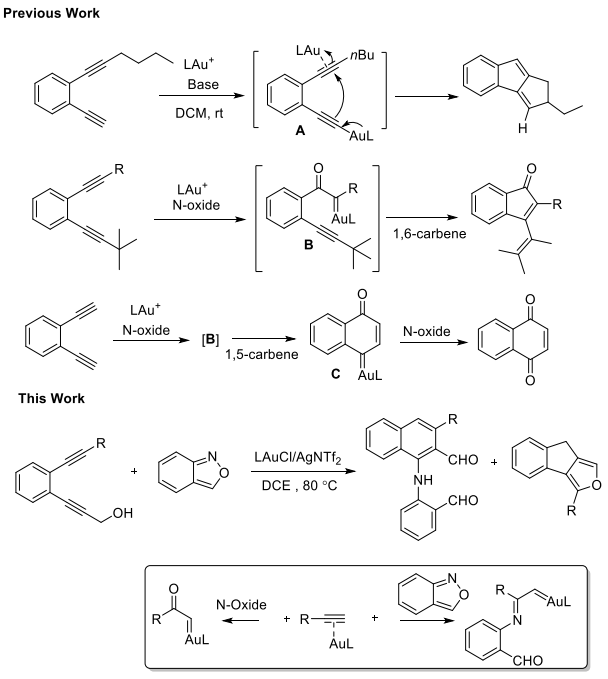
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201######.((Please delete if not appropriate))

**Abstract.** Gold-catalyzed aminoaromatizations of 1,n-diynes with anthranils afforded 1-amino-2-napthaldehyde derivatives efficiently. In this reaction sequence, anthranils preferably attack at gold-coordinated prop-3-yn-1-ols to generate α-imino gold carbenes that enable subsequent cyclizations with the other alkynes. Chemical functionalizations of the resulting 1-amino-2-napthaldehydes are presented to manifest the synthetic utility of these reactions.

**Keywords:** Aminoaromatizations; amino-napthaldehyde derivatives; α-imino gold carbenes; anthranils; 1,2-bis(alkynyl)benzenes; 1, n diynes.

## Introduction

Catalytic transformations of 1,*n*-diynes into various carbo- or heterocycles with homogeneous gold catalysts has become an inspiring topic in organic synthesis.[1] Numerous useful reactions have been developed with 1,*n*-diynes, including [4+n] annulations (n = 1 and 2)[2], cycloisomerizations[3], bicyclic annulations[4] and polyaromatization reactions[5]. In the context of 1,2-bis(alkynyl)benzenes, Zhang[6] and Hashmi[7] independently reported novel gold-catalyzed cycloisomerizations beyond the well-known Berman reactions, further yielding 1,2-dihydrocyclopenta[*a*]indenes; this notable process involves initial digold intermediates to induce intramolecular cyclizations to generate gold vinylidene intermediates (Eq.1)[6,7]. Apart from these cycloisomerizations, Hashmi reported gold-catalysed oxidative cyclisation of these 1,2-bis(alkynyl)benzenes using pyridine-based-N-oxides to generate α-oxo carbenes to allow a subsequent 1,6-carbene shift before preceeding to substituted indenones (Eq.2)[7a]. Ye reported gold-catalyzed oxidative cyclizations of terminal 1,2-bis(alkynyl)benzenes, followed by a 1,5-carbene shift to form vinylgold carbenes, which undergo second oxidations to deliver 1,4-napthaquinone derivatives (Eq. 3)[8].

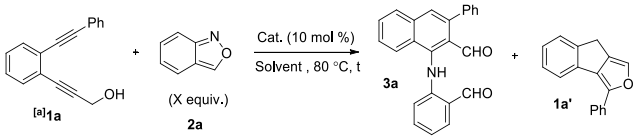



We are aware of no reports of intramolecular cyclizations of 1,2-bis(alkynyl)benzenes via α-imino metal carbenes. In gold catalysis, α-imino gold carbenes could be generated from the reactions of anthranils with reactive alkynes such as ynamides,[9] propiolates[10] or alkynols,[11] in a pattern analogous to the alkyne oxidations with *N*-oxides to generate α-oxo gold carbenes. Within our continuing interest in

anthranil chemistry,[9-11] this work reports gold-catalyzed aminoaromatization of 1,2-bis(alkynyl)benzenes with anthranils, efficiently affording 1-amino-2-napthaldehyde derivatives (Eq. 4). The synthetic utility of these resulting products is demonstrated here.

## Result and Discussion

**Table 1.** Optimization of the reaction conditions.

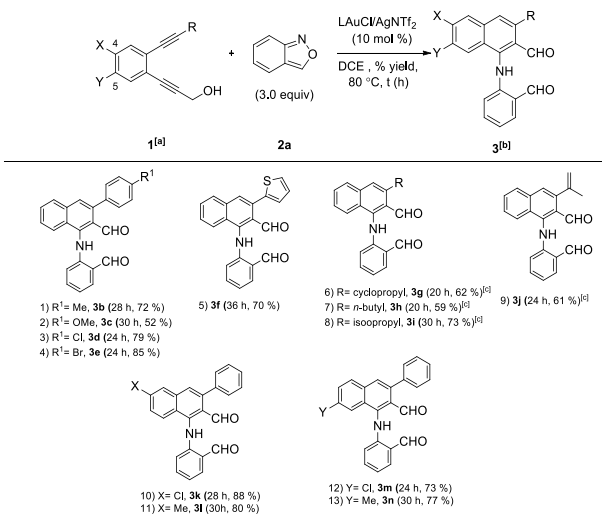



| Entry | Catalyst | Solvent | 2a (equiv) | t (h) | Yield (%)[b] 1a | 3a | 1a' |
|---|---|---|---|---|---|---|---|
| 1 | $PPh_3AuCl/AgNTf_2$ | DCE | 3 | 36 | 80 | 15 | 0 |
| 2 | $(PhO)_3PAuCl/AgNTf_2$ | DCE | 3 | 24 | 95 | 0 | 0 |
| 3 | $IPrAuCl/AgNTf_2$ | DCE | 3 | 30 | 15 | 22 | 61 |
| 4 | $LAuCl/AgNTf_2$ | DCE | 3 | 24 | 0 | 62 | 28 |
| 5[c] | $LAuCl/AgNTf_2$ | DCE | 3 | 24 | 0 | 79 | 0 |
| 6 | $LAuCl/AgNTf_2$ | DCE | 1.5 | 24 | 0 | 58 | 35 |
| 7 | LAuCl/AgOTf | DCE | 3 | 30 | 80 | 10 | 0 |
| 8 | $LAuCl/AgSbF_6$ | DCE | 3 | 20 | 0 | 15 | 75 |
| 9 | $AuCl_3$ | DCE | 3 | 24 | 95 | 0 | 0 |
| 10 | $AgNTf_2$ | DCE | 3 | 24 | 99 | 0 | 0 |
| 11 | $LAuCl/AgNTf_2$ | Toulene | 3 | 24 | 0 | 38 | 58 |
| 12 | $LAuCl/AgNTf_2$ | 1,4-dioxane | 3 | 24 | 53 | 12 | 30 |
| 13 | $LAuCl/AgNTf_2$ | THF | 3 | 24 | 80 | 0 | 15 |
| 14 | $LAuCl/AgNTf_2$ | DCE | 0 | 24 | 0 | 0 | 75 |

[a] **1a** = 0.08M. [b] Product yields are obtained after purification from a silica column, IPr = 1,3-bis(diisopropylphenyl)imidazol-2-ylidene, L = P(*t*-Bu)$_2$(*o*-biphenyl), [c] **1a** = 0.17 M, DCE = 1,2-dichloroethane.

Table 1 shows the optimized conditions for gold-catalyzed intramolecular cyclizations of 1,2-bis(alkynyl)benzene **1a** with anthranil **2a** using various gold catalysts. Substrate **1a** is designed to bear a prop-1-yn-1-ol[11] to increase its reactivity toward anthranils when gold catalyst is present. We observed no reactivity for those 1,2-bis(alkynyl)benzenes bearing only unfunctionalized terminal or internal alkynes as in eq 1-4. We first employed $PPh_3AuCl/AgNTf_2$ and $(PhO)_3PAuCl/AgNTf_2$ to run the reaction of 1,2-bis(alkynyl)benzene **1a** (0.08 M) with anthranil **2a** (3 equiv) in hot DCE (80 $^0$C), but these catalysts led to 80-95 % recovery of starting material **1a** (entries 1-2); herein, we were able to obtain our target **3a** in 15 % yield (entry 1). With $IPrAuCl/AgNTf_2$, the yield of compound **3a** was slightly increased to 22 % yield, albeit with a cycloisomerization product **1a'** in 61 % yield (entry 3). To our pleasure, the chemoselectivity was greatly improved with $LAuCl/AgNTf_2$ (L= P(*t*-Bu)$_2$(*o*-biphenyl) to afford desired **3a** in 62% yield (entry 4). With diyne **1a** at a high concentration (0.17 M), we increased the yield of compound **3a** to 79 % with byproduct **1a'** in a negligible proportion (entry 5); herein, a small loading (1.5 equiv.) of anthranil **2a** regenerated the by product in 35% yield (entry 6). For P(*t*-Bu)$_2$(*o*-biphenyl)AuCl, various silver salts such as AgOTf and $AgSbF_6$ led to formation of **3a** in diminished yields (10-15%, entries 7-8). $AuCl_3$ and $AgNTf_2$ were catalytically inactive to give starting **1a** with a high recovery (entries 9-10). We evaluated also the activity of P(t-Bu)$_2$(*o*-biphenyl)$AuCl/AgNTf_2$ in different solvents; the yields of compound **3a** were as follows: 38 % in toluene, 12 % in 1,4-dioxane and 0% in THF (entries 11-13). In the absence of anthranil **2a** (n = 0), P(t-Bu)$_2$(*o*-biphenyl)$AuCl/AgNTf_2$ efficiently delivered an cycloisomerization product **1a'** in 75% yield ( entry 14). The molecular structure of our target **3a** is inferred from X-ray diffraction of its relative **4f** (vide infra).[12]

**Table 2.** Catalytic reactions on various 1,2-bis(alkynyl)benzenes.



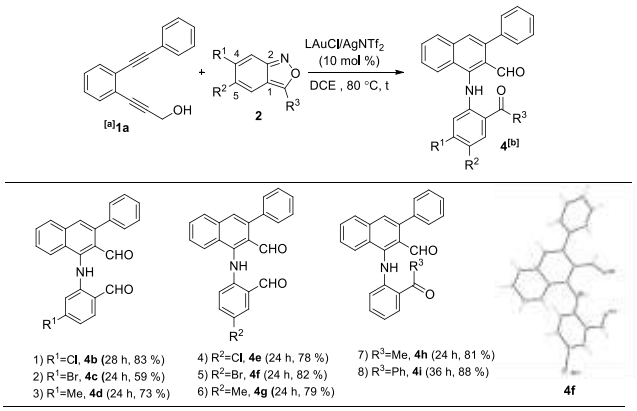

[a]**1a** = 0.17 M L = P(t-Bu)$_2$(*o*-biphenyl). [b]Product yields are reported after purification from a silica gel column. [c]reaction temperature = 40 °C.

We assessed the substrate scope of these new aminoaromatizations on various 1,2-bis(alkynyl)benzene **1a-1n**; the reactions were operated under the standard condition in Table 1 (entry 5); a summary of the results is provided in Table 2. We tested the reactions on several 1,2-bis(alkynyl)benzene **1b-1e** bearing various arylalkyne substituents, R =4-X$C_6H_4$ ($R_1$ = Me, OMe, Cl, Br), further affording 1-amino-2-napthaldehydes **3b-3e** in 52-85 % yields with the methoxy derivative **3c** being less efficient (entries 1-4). For this methoxy product **3c**, we speculate that gold catalyst coordinates strongly with this electron-rich alkyne, which is however not the active site for the reactions. For 2-thienyl-substituted diynes **1f**, this aminoaromatization product **3f** was obtained in 70% yield (entry 5). We varied these internal alkynes with alkyl as in 1,2-bis(alkynyl)benzene **1g-1i**; (R = cyclopropyl, *n*-butyl and isopropyl), furnishing 1-amino-2-napthaldehyde derivatives **3g-3i** in 59-73% yields (entries 6-8).

10.1002/adsc.202000591

Vinylalkyne deivative **1j** was also amenable to this aminoaromatization to afford product **3j** in 61% yield (entry 9). The scope of substrates was further expanded with additional C(4)-substituents (X = Cl and Me) at the bridging benzene of 1,2-bis(alkynyl)benzene **1k-1l**, producing compounds **3k-3l** in 80-88 % yields (entries 10-11). For diynes **1m-1n** bearing C-(5) substituents (Y=Cl and Me), their gold-catalyzed reactions furnished 1-amino-2-napthaldehydes **3m-3n** in 73-77 % yields (entries 12-13).

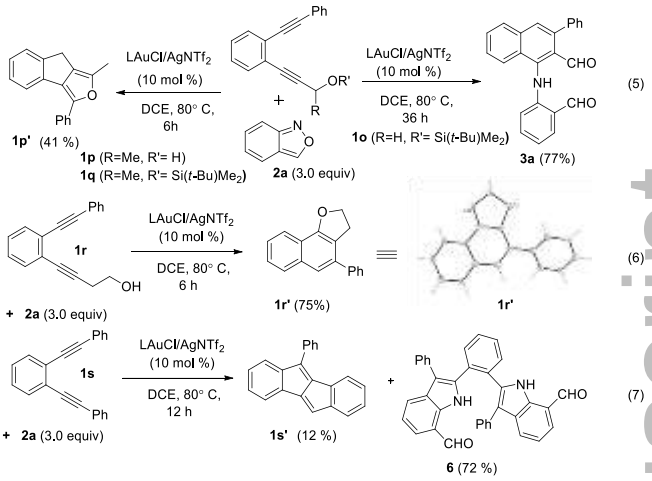
**Table 3.** Reactions on various substituted Benzisoxazoles



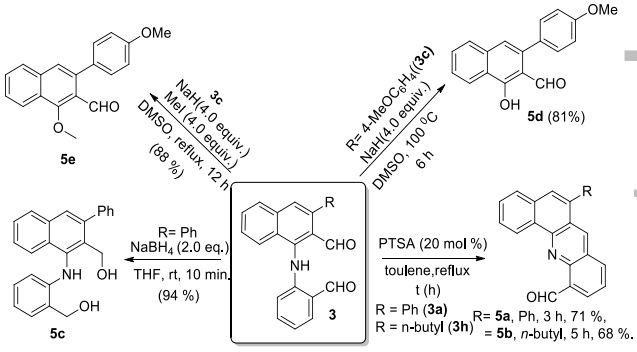

[a]**1a** = 0.17 M. **2** = 3.0 equiv. L = P(t-Bu)$_2$(*o*-biphenyl).
[b]Product yields are reported after purification from a silica gel column. DCE = 1,2-dichloroethane.

We also assess the reaction generality with various anthranils **2b-2d** under standard conditions; the results are provided in Table 3. We tested the reactions of anthranils **2b-2d** bearing various C(4)-substituents (R$^1$ = Cl, Br and Me), further affording 1-amino-2- napthaldehydes **4b-4d** in 59-83 % yields (entries 1-3). In the case of C(5)-substituted anthranils **2e-2g** (R$^2$ = Cl, Br and Me), their resulting products **4e-4g** were obtained in satisfactory yields (78-82 %, entries 4-6); the molecular structure of compound **4f** was determined with x-ray diffraction. We prepared anthranils **2h-2i** with a methyl and phenyl substituent at the nitroxy ring, (R$^3$= Me and Ph), delivering 1-amino-2-napthaldehydes **4h** and **4i** efficiently (entries 7-8).

To clarify the role of a free hydroxyl group on the reaction chemoselectivity, we prepared diyne **1o** bearing a siloxy-protected but-1-ynol, that still yielded the aminocyclization product **3a** in 77% yield (eq 5). This information indicates that a free alcohol is not crucial to affect this aminocyclization reactivity. We also prepared diyne **1p** bearing a 2-methylprop-1-yn-3-ol and siloxy protected 2-methylprop-1-yn-3-ol, diyne **1q** which yielded only the cycloisomerization product **1p**' in 41% yield (eq 5).We tested the reaction on diyne **1r** bearing a but-1-yn-4-ol that delivered only the cycloisomerization product **1r'** (89 %, eq 6); its molecular structure was characterized by X-ray diffraction.[12] We prepared diyne **1s** to check the reaction generality towards anthranil **2a** in standard reaction condition, we obtained the self cycloisomerization product **1s'** in 12 % yield, and a doubly annulated indole product **6** in 72 % (eq. 7)[15-a,b]. We believe that the superior reactivity of Au-π prop-1-yn-3-ol (**1a**) and its siloxy derivative **1o** toward anthranils, as compared to 3-methyl-1-propynol (**1p**) and 1-butun-4-ol (**1r**) is due to the greater electron-withdrawing power of prop-1-yn-3-ol. Without this alcohol, diyne **1s** followed the formation of indole according to a known pathway.[15b]




Scheme 1 demonstrates chemical functionalizations of some resulting products **3**. Treatment of two representatives **3a** (R = Ph) and **3h** (R = *n*-Bu) with *p*-toulenesulfonic acid (20 mol %) in hot toluene (80 $^0$C, 3 h) afforded polyaromatic derivatives **5a** (R = Ph) and **5b** (R = *n*-butyl) in 68-71% yields. Compound **3a** was further reduced by



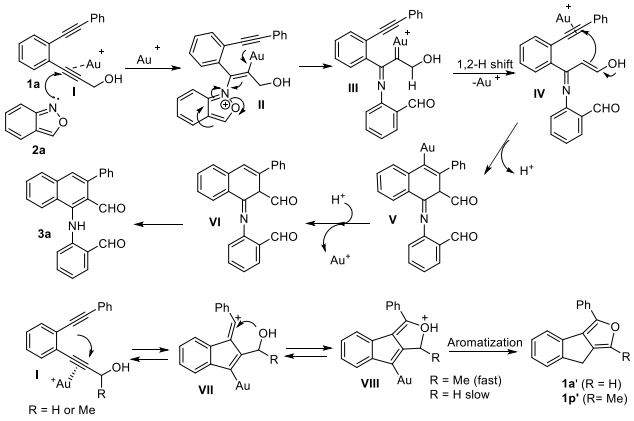

**Scheme 1.** Functionalizations with 1-amino-nathaldehyde derivatives **3.**

$NaBH_4$ in THF to deliver a diol compound **5c** in 94% yield**.** Treatment of compound **3c** (R = 4-MeOC$_6$H$_4$) with NaH in hot DMSO (100 $^0$C, 6 h) enabled an unexpected deamination reaction, producing an phenol derivative **5d** in 81 % of which $^1$H and $^{13}$C NMR are identical to an authentic sample reported in the literature[13,14]**.** If MeI (4.0 equiv) was present in this NaH-promoted deamination reaction**,** a methyl phenoxy product **5e** was obtained in 88% yield**.** The mechanism of formation of compounds **5d** and **5e** are not difficult to elucidate.[14]

We postulate a mechanism for the aminocyclizations of bis(alkynyl)benzenes **1** with anthranils (Scheme 2); the reactions begin with the

coordination of gold complex with a prop-1-yn-3-ol moiety. As shown in our previous work, gold-π-prop-1-yn-3-ol has a strong affinity toward anthranils because of the electron-withdrawing property of a hydroxyl group. This *N*-attack of anthranil is expected to yield α-imino gold carbenes **III** that is typically terminated by a 1,2-hydride migration, releasing gold complex and α,β-unsaturated 3-hydroxy-enimines **IV.** A subsequent cyclization of intermediate **IV** via a 6-exo dig mode yields gold-containing naphthalene-1-(2*H*)-imine, which undergoes protodeauration to produce species **VI;** a further aromatization of this species forms our observed product **3a.** In this mechanism, a alkyne/carbene metathesis process is not occurring for gold carbene **III** because a competitive 1,2-hydride shift is known to be very facile with a low barrier.

In the absence of anthranil**,** these bis(alkynyl)benzenes yield cycloisomerization by products **1a'** and **1q'** instead**.** In these cases**,** π-prop-1-yn-3-ol **1a** will be attacked by a phenylacetylene to furnish an intramolecular cyclization, further producing intermediate **VII** and oxonium species **VIII** sequentially**.** We believe that formation of compound **1p'** (R = Me) is more rapid than its unsubstituted analogue **1a** (R = H) because its corresponding oxonium species **VIII** is stabilized efficiently by a methyl group. Accordingly, formation of compound **1p'**. (R = Me) is not easily impeded by anthranil **2a**.




**Scheme 2**. A Plausible reaction mechanism

## Conclusion

In summary, We report new aminocyclizations of bis(alkynyl)benzenes with anthranils to afford 1-amino-2-napthaldehyde derivatives efficiently. These catalytic reactions are applicable bis(alkynyl)benzenes and anthranils over a wide scope. On the basis of our control experiments, we postulate that this reaction sequence involves an initial attack of anthanils at gold-π-prop-1-yn-3-ols of diynes, leading to a formation of α-imino gold carbenes before preceeding to a 6-endo cyclizations of the other alkynes. Various chemical functionalizations of these resulting 1-amino-2-napthaldehydes have been performed to highlight the synthetic utility of this new catalysis.

## Experimental Section

**Standard procedure for the synthesis of 1-((2-formylphenyl)amino)-3-phenyl-2-naphthaldehyde (3a):** A catalytic tube was charged with LAuCl (14 mg, 0.025 mmol) and $AgNTf_2$ (10 mg, 0.025mmol), and this mixture was added dry DCE (0.5 ml) under $N_2$ atmosphere. The resulting mixture was stirred at 25 °C for 10 min. To this mixture was added a dry DCE solution of 3-(2-(phenylethynyl)phenyl)prop-2-yn-1-ol (**1a**) (0.06 mg, 0.258 mmol) and benzo[*c*]isoxazole (**2a**) (92 mg, 0.774 mmol) in 1.0 mL DCE. After stirring at 80 °C for 24 h, the reaction mixture was filtered over a short celite bed, concentrated, and eluted through a silica column (5% EA/hexane) to give the desired 1-((2-formylphenyl)amino)-3-phenyl-2-naphthaldehyde (**3a**) (0.071 mg, 0.196 mmol, 79%) as yellow sticky liquid.

## Characterization

**Spectral data for 1-((2-formylphenyl)amino)-3-phenyl-2-naphthaldehyde (3a):**
Yellow sticky liquid; 71 mg, 79%. $^1$H NMR (500 MHz, $CDCl_3$): δ 11.21 (s, 1H), 10.10 (s, 1H), 9.99 (s, 1H), 7.96 (d, *J* = 7.0 Hz, 1H), 7.87 (d, *J* = 8.5 Hz, 1H), 7.70 (s, 1H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.60 (t, *J* = 7.5 Hz, 1H), 7.48-7.39 (m, 6H), 7.17 (t, *J* = 7.5 Hz 1H), 6.88 (t, *J* = 7.0 Hz, 1H), 6.38 (d, *J* = 8.5 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 193.8, 192.6, 147.8, 141.1, 139.2, 138.9, 135.9, 135.8, 134.9, 129.9, 129.2, 128.5, 128.4, 128.1, 127.9, 127.1, 126.6, 126.3, 125.8, 120.9, 118.6, 115.3; EI-MS calcd for $C_{24}H_{17}NO_2$: 351.1259, found: 351.1262.

**Spectral data for 1-((2-formylphenyl)amino)-3-(*p*-tolyl)-2-naphthaldehyde (3b):**
Yellow solid; 64 mg, 72%. $^1$H NMR (600 MHz, $CDCl_3$): δ 11.19 (s, 1H), 10.10 (s, 1H), 9.99 (s, 1H), 7.95 (d, *J* = 8.4 Hz, 1H), 7.86 (d, *J* = 8.4 Hz, 1H), 7.69 (s, 1H), 7.64 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.60-7.57 (m, 1H), 7.41-7.38 (m, 1H), 7.32 (d, *J* = 7.8 Hz, 2H), 7.27 (d, *J* = 7.8 Hz, 2H), 7.16 (td, *J* = 7.2, 1.2 Hz, 1H), 6.87 (t, *J* = 7.8 Hz, 1H), 6.37 (d, *J* = 8.4 Hz, 1H), 2.42 (s, 3H) ; $^{13}$C NMR (150 MHz, $CDCl_3$): δ 193.8, 192.7, 147.9, 141.2, 139.0, 137.8, 135.9, 135.8, 134.8, 129.8, 129.2, 129.1, 128.5, 128.0, 126.9, 126.5, 126.3, 125.9, 120.8, 118.5, 115.3, 21.2, one 'C' merged with others; EI-MS calcd for $C_{25}H_{19}NO_2$: 365.1416, found: 365.1414.

**Spectral data for 1-((2-formylphenyl)amino)-3-(4-methoxyphenyl)-2-naphthaldehyde (3c):**
Yellow sticky liquid; 45 mg, 52%. $^{1}$H NMR (600 MHz, $CDCl_3$): δ 11.18 (s, 1H), 10.10 (s, 1H), 9.99 (s, 1H), 7.94 (d, *J* = 9.0 Hz, 1H), 7.85 (d, *J* = 8.4 Hz, 1H), 7.68 (s, 1H), 7.64 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.59-7.57 (m, 1H), 7.40-7.35 (m, 3H), 7.16 (t, *J* = 9.0 Hz, 1H), 6.99 (d, *J* = 8.4 Hz, 2H), 6.87 (t, *J* = 7.8 Hz, 1H), 6.36 (t, *J* = 8.4 Hz, 1H), 3.86 (s, 3H) ; $^{13}$C NMR (150 MHz, $CDCl_3$): δ 193.8, 192.8, 159.5, 147.9, 140.8, 138.9, 135.9, 135.8, 134.8, 131.1, 130.0, 129.1, 128.5, 127.9, 126.9, 126.4, 126.3, 126.0, 120.8, 118.5, 115.3, 114.0, 55.4; EI-MS calcd for $C_{25}H_{19}NO_3$: 381.1365, found: 381.1362.

**Spectral data for 3-(4-chlorophenyl)-1-((2-formylphenyl)amino)-2-naphthaldehyde (3d):**
Yellow Solid; 67 mg, 79%. $^{1}$H NMR (500 MHz, $CDCl_3$): δ 11.15 (s, 1H), 10.09 (s, 1H), 10.02 (s, 1H), 7.96 (d, *J* = 8.5 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.65-7.58 (m, 5H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.30 (t, *J* = 8.0 Hz, 2H), 7.17 (t, *J* = 8.0 Hz, 1H), 6.88 (t, *J* = 7.5 Hz, 1H), 6.37 (d, *J* = 8.0 Hz, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 193.9, 192.1, 147.9, 139.8, 139.6, 138.0, 136.0, 135.8, 134.9, 131.6, 131.3, 129.6, 128.6, 128.4, 127.2, 126.9, 126.1, 125.8, 122.2, 120.7, 118.7, 115.1; EI-MS calcd for $C_{24}H_{16}ClNO_2$: 385.0870, found: 385.0874.

**Spectral data for 3-(4-bromophenyl)-1-((2-formylphenyl)amino)-2-naphthaldehyde (3e):**
Yellow Solid; 69 mg, 85%. $^{1}$H NMR (600 MHz, $CDCl_3$): δ 11.14 (s, 1H), 10.09 (s, 1H), 10.02 (s, 1H), 7.96 (d, *J* = 8.4 Hz, 1H), 7.86 (d, *J* = 8.4 Hz, 1H), 7.66-7.64 (m, 2H), 7.62-7.58 (m, 3H), 7.44-7.41 (m,1H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.17 (td, *J* = 8.4, 1.2 Hz, 1H), 6.88 (t, *J* = 7.8 Hz, 2H), 6.37 (d, *J* = 8.4 Hz, 1H); $^{13}$C NMR (150 MHz, $CDCl_3$): δ 193.9, 192.1, 147.8, 139.7, 139.6, 138.0, 136.0, 135.8, 134.9, 131.6, 131.3, 129.5, 128.6, 128.4, 127.2, 126.9, 126.1, 125.8, 122.2, 120.7, 118.7, 115.1; EI-MS calcd for $C_{24}H_{16}BrNO_2$: 421.0364, found: 421.0365.

**Spectral data for 1-((2-formylphenyl)amino)-3-(thiophen-2-yl)-2-naphthaldehyde (3f):**
Yellow liquid; 62 mg, 70%. $^{1}$H NMR (600 MHz, $CDCl_3$): δ 11.18 (s, 1H), 10.12 (s, 1H), 10.10 (s, 1H), 7.94 (d, *J* = 8.4 Hz, 1H), 7.86 (dd, *J* = 7.8, 0.6 Hz, 1H), 7.82 (s, 1H), 7.64 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.60-7.58 (m, 1H), 7.43-7.39 (m, 2H), 7.18-7.13 (m, 2H), 7.08 (dd, *J* = 3.6, 1.2 Hz, 1H), 6.88 (td, *J* = 7.2, 1.2 Hz, 1H), 6.36 (d, *J* = 7.0 Hz, 1H); $^{13}$C NMR (150 MHz, $CDCl_3$): δ 193.7, 192.3, 147.7, 139.9, 139.1, 135.9, 135.6, 134.8, 133.3, 129.3, 129.1, 128.6, 128.3, 127.8, 127.7, 126.9, 126.8, 126.4, 125.9, 120.9, 118.7, 115.4; EI-MS calcd for $C_{22}H_{15}NO_2S$: 357.0823, found: 357.0825.

**Spectral data for 3-cyclopropyl-1-((2-formylphenyl)amino)-2-naphthaldehyde (3g):**
Yellow liquid; 60 mg, 62%. $^{1}$H NMR (600 MHz, $CDCl_3$): δ 10.68 (s, 1H), 10.64 (s, 1H), 10.06 (s, 1H), 7.90 (d, *J* = 8.4 Hz, 1H), 7.71 (d, *J* = 7.8 Hz, 1H), 7.63 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.54 (t, *J* = 7.8 Hz, 1H), 7.49 (s, 1H), 7.37 (t, *J* = 7.8 Hz, 1H), 7.18 (dt, *J* = 8.4, 1.2 Hz, 1H), 6.84 (t, *J* = 7.8 Hz, 1H), 6.32 (d, *J* = 8.4 Hz, 1H), 2.65-2.60 (m, 1H), 1.07 (s, 2H), 0.85 (t, *J* = 7.2 Hz, 2H); $^{13}$C NMR (150 MHz, $CDCl_3$): δ 194.3, 193.5, 149.2, 140.8, 140.5, 136.5, 136.1, 135.5, 129.1, 129.0, 128.4, 127.9, 126.4, 124.8, 124.0, 119.8, 118.0, 114.2, 13.7, 8.1; EI-MS calcd for $C_{21}H_{17}NO_2$: 315.1259, found: 315.1262.

**Spectral data for 3-butyl-1-((2-formylphenyl)amino)-2-naphthaldehyde (3h):**
Yellow liquid; 54 mg, 59%. $^{1}$H NMR (600 MHz, $CDCl_3$): δ 10.48 (s, 1H), 10.45 (s, 1H), 10.05 (s, 1H), 7.92 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.80 (d, *J* = 8.4 Hz, 1H), 7.62 (dd, *J* = 7.8, 1.8 Hz, 2H), 7.58-7.55 (m, 1H), 7.40-7.38 (m, 1H), 7.21-7.18 (m, 1H), 6.83 (td, *J* = 7.2, 0.6 Hz, 1H), 6.31 (d, *J* = 8.4 Hz, 1H), 3.16-3.06 (m, 2H), 1.66-1.61 (m, 2H), 1.47-1.41 (m, 2H), 0.95 (t, *J* = 7.8 Hz, 3H); $^{13}$C NMR (150 MHz, $CDCl_3$): δ 194.5, 193.2, 149.8, 141.4, 140.5, 136.6 136.2, 135.8, 129.2, 128.9, 128.8, 127.9, 127.8, 126.5, 124.2, 119.3, 117.8, 113.7, 33.9, 33.5, 22.7, 13.9; EI-MS calcd for $C_{22}H_{21}NO_2$: 331.1572, found: 331.1559.

**Spectral data for 1-((2-formylphenyl)amino)-3-isopropyl-2-naphthaldehyde (3i):**
Yellow liquid; 70 mg, 73%. $^{1}$H NMR (600 MHz, $CDCl_3$): δ 10.51 (s, 1H), 10.41 (s, 1H), 10.05 (s, 1H), 7.92 (d, *J* = 8.4 Hz, 1H), 7.83 (d, *J* = 7.8 Hz, 1H), 7.78 (s, 1H), 7.62 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.58-7.56 (m, 1H), 7.41-7.39 (m, 1H), 7.21-7.18 (m, 1H), 6.84-6.82 (m, 1H), 6.30 (d, *J* = 9.0 Hz, 1H), 3.99-3.92 (m, 1H), 1.36 (dd, *J* = 43.2, 6 Hz, 6H); $^{13}$C NMR (150 MHz, $CDCl_3$): δ 194.5, 193.8, 149.8, 146.4, 140.8, 136.7, 136.2, 135.8, 129.1, 128.7, 128.1, 126.6, 123.9, 123.7, 119.3, 117.8, 113.6, 28.4, 24.2, 23.8; EI-MS calcd for $C_{21}H_{19}NO_2$: 317.1416, found: 317.1413.

**Spectral data for 1-((2-formylphenyl)amino)-3-(prop-1-en-2-yl)-2-naphthaldehyde (3j):**
Yellow liquid; 59 mg, 61%. $^{1}$H NMR (600 MHz, $CDCl_3$): δ 10.94 (s, 1H), 10.29 (s, 1H), 10.08 (s, 1H), 7.92 (d, *J* = 8.4 Hz, 1H), 7.83 (d, *J* = 7.8 Hz, 1H), 7.63 (d, *J* = 7.8 Hz, 1H), 7.60 (s, 1H), 7.57 (t, *J* = 7.2 Hz, 1H), 7.38 (t, *J* = 7.2 Hz, 1H), 7.16 (t, *J* = 7.2 Hz, 1H), 6.86 (t, *J* = 7.2 Hz, 1H), 6.32 (d, *J* = 9.0 Hz, 1H), 5.35 (s,1H), 5.02 (s, 1H), 2.18 (s, 3H); $^{13}$C NMR (150 MHz, $CDCl_3$): δ 193.9, 192.4, 148.4, 144.2, 142.6, 139.6, 136.2, 136.0, 135.1, 129.1, 128.5, 128.3, 126.6,

126.1, 125.7, 125.4, 120.4, 118.3, 117.1, 114.8, 25.1; EI-MS calcd for $C_{22}H_{17}NO_2$: 315.1259, found: 315.1253.

**Spectral data for 6-chloro-1-((2-formylphenyl)amino)-3-phenyl-2-naphthaldehyde (3k):**

Yellow sticky liquid; 75mg, 88%. $^1$H NMR (600 MHz, $CDCl_3$): δ 11.11 (s, 1H), 10.09 (s, 1H), 9.96 (s, 1H), 7.93 (s, 1H), 7.82 (d, *J* = 9.0 Hz, 1H), 7.69 (s, 1H), 7.66 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.53 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.48-7.40 (m, 5H), 7.21-7.18 (m, 1H), 6.90 (td, *J* = 7.8, 0.6 Hz, 1H), 6.33 (d, *J* = 8.4 Hz, 1H); $^{13}$C NMR (150 MHz, $CDCl_3$): δ 193.9, 192.3, 147.5, 141.5, 138.4, 138.1, 136.2, 135.0, 133.9, 132.9, 130.1, 129.8, 129.2, 128.6, 128.1, 126.9, 126.8, 125.0, 120.8, 118.8, 114.8, one 'C' merge with others; EI-MS calcd for $C_{24}H_{16}ClNO_2$: 385.0870, found: 385.0866.

**Spectral data for 1-((2-formylphenyl)amino)-6-methyl-3-phenyl-2-naphthaldehyde (3l):**

Yellow Solid; 71 mg, 80%. $^1$H NMR (500 MHz, $CDCl_3$): δ 11.27 (s, 1H), 10.13 (s, 1H), 10.01 (s, 1H), 7.88 (d, *J* = 8.5 Hz, 1H), 7.77 (d, *J* = 9.5 Hz, 2H), 7.63 (s, 1H), 7.51-7.43 (m, 5H), 7.26 (d, *J* = 8.5 Hz, 1H), 7.20 (t, *J* = 7.5 Hz, 1H), 6.90 (t, *J* = 7.5 Hz, 1H), 6.43 (d, *J* = 8.5 Hz, 1H), 2.54 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 193.7, 192.6, 147.7, 141.3, 139.6, 139.2, 139.0, 136.1, 135.9, 134.8, 129.8, 128.8, 128.4, 127.8, 127.5, 126.3, 126.1, 124.8, 120.9, 118.5, 115.4, 21.8, One 'C' mergerd with others; EI-MS calcd for $C_{25}H_{19}NO_2$: 365.1416, found: 365.1414.

**Spectral data for 7-chloro-1-((2-formylphenyl)amino)-3-phenyl-2-naphthaldehyde (3m):**

Yellow sticky liquid; 62 mg, 73%. $^1$H NMR (500 MHz, $CDCl_3$): δ 11.11 (s, 1H), 10.09 (s, 1H), 9.96 (s, 1H), 7.93 (s, 1H), 7.82 (d, *J* = 8.5 Hz, 1H), 7.69 (s, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.53 (d, *J* = 8.5 Hz, 1H), 7.48-7.41 (m, 5H), 7.20 (d, *J* = 7.5 Hz, 1H), 6.90 (t, *J* = 7.5 Hz, 1H), 6.33 (d, *J* = 8.5 Hz, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 193.9, 192.3, 147.5, 141.5, 138.4, 138.1, 136.2, 135.0, 133.9, 132.9, 130.1, 129.8, 129.2, 128.6, 128.1, 126.9, 126.8, 125.0, 120.8, 118.8, 114.8, one 'C' merge with others; EI-MS calcd for $C_{24}H_{16}ClNO_2$: 385.0870, found: 385.0871.

**Spectral data for 1-((2-formylphenyl)amino)-7-methyl-3-phenyl-2-naphthaldehyde (3n):**

Yellow Solid; 68 mg, 77%. $^1$H NMR (500 MHz, $CDCl_3$): δ 11.08 (s, 1H), 10.10 (s, 1H), 9.99 (s, 1H), 7.77 (d, *J* = 8.5 Hz, 1H), 7.73 (s, 1H), 7.67 (s, 1H), 7.64 (d, *J* = 7.0 Hz, 1H), 7.47-7.39 (m, 6H), 7.17 (t, *J* = 7.5 Hz, 1H), 6.86 (t, *J* = 7.5 Hz, 1H), 6.36 (d, *J* = 8.5 Hz, 1H), 2.39 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 193.9, 192.6, 148.1, 140.1, 139.0, 138.4, 136.8, 136.0, 134.9, 134.1, 131.6, 129.8, 128.6, 128.4, 128.3, 127.7, 127.1, 126.2, 124.9, 120.6, 118.2, 114.9, 21.9; EI-MS calcd for $C_{25}H_{19}NO_2$: 365.1416, found: 365.1420.

## Acknowledgements

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

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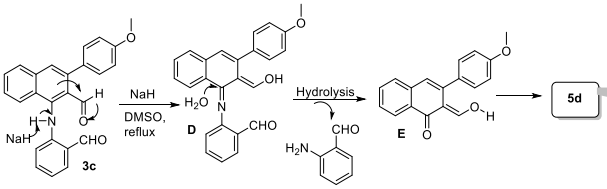
[14] The mechanism of formation of the deamination product **5d** is provided in a postulated mechanism below. An N-H deprotonation of species **3c** with NaH generates an imino intermediate **D** which undergoes hydrolysis to release the 2-aminobenzaldehyde together and new intermediate **E**. A subsequent tautomerization of this species is expected to yield 1-hydroxy-formylnathphalene **5d.**

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10.1002/adsc.202000591

FULL PAPER

# Gold-Catalyzed Aminoaromatizations of 1,2-Bis(alkynyl)benzenes with Anthranils to Yield 1-Amino-2-napthaldehyde Products

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Yashwant Bhaskar Pandit and Rai-Shung Liu*