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# Gold-Catalyzed Carboalkoxylations of 2-Ethynylbenzyl Ethers to form 1- and 2-Indanones Chemoselectively: Effects of Ligands and Solvents

Chiou-Dong Wang,[a] Yi-Feng Hsieh,[a] and Rai-Shung Liu[a,*]

[a] Department of Chemistry, National Tsing-Hua University, Hsinchu, Taiwan, ROC
Fax: (+886)-3-571-1082; e-mail: rsliu@mx.nthu.edu.tw

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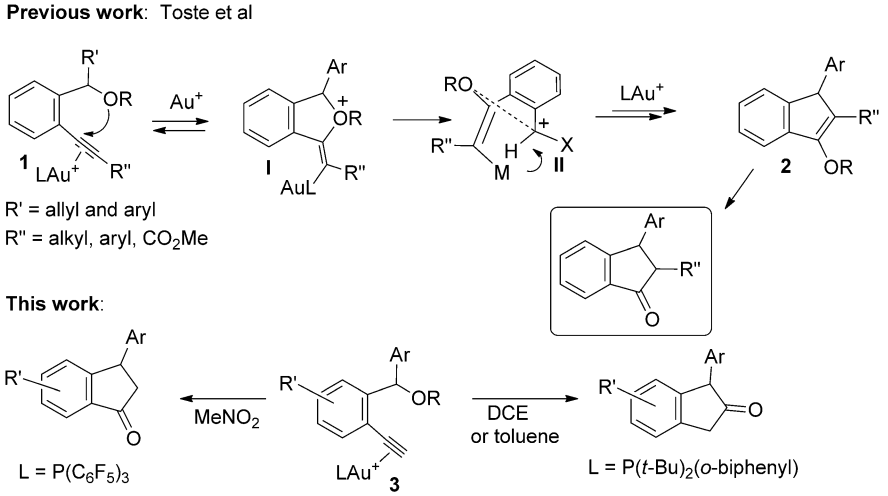
**Abstract:** The selective syntheses of 1- and 2-indanone compounds from 2-ethynylbenzyl ethers have been achieved with suitable catalysts and solvents. The highly acidic [tris(pentafluorophenyl)phosphine]gold hexafluoroantimonate [$P(C_6F_5)_3AuSbF_6$] in nitromethane ($MeNO_2$) preferably gives 1-indanones whereas [(*ortho*-biphenyl)di(*tert*-butyl)phosphine]gold triflimide [$P(tBu)_2(o$-biphenyl)$AuNTf_2$] in dichloroethane tends to form 2-indanone derivatives. For 2-indanone products, we isolated two indenyl methyl ethers for deuterium labeling analyses, providing evidence for π-alkyne activation.

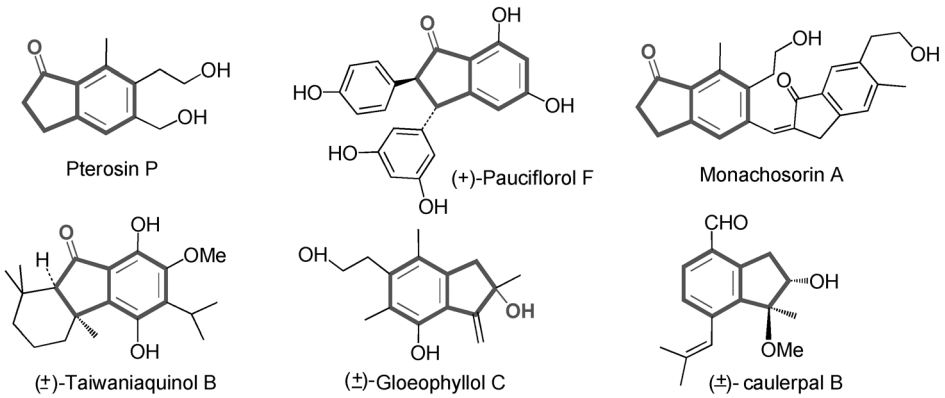
**Keywords:** carboalkoxylations; 2-ethynylbenzyl ethers; gold catalysis; 1-indanones; 2-indanones

The Au- and Pt-catalyzed electrophilic activations of alkynes offer convenient tools to mediate the formation of various C–X bonds (X = C, O, N), thus providing access to 1,2-difunctionalized molecules.[1] The carboalkoxylation reactions of alkynes emerge as a thriving topic, which enable new C–C and C–O bonds to be generated on to readily available alkynes.[2–4] Toste and co-workers reported the carboalkoxylations of 2-alkynylbenzyl ethers, involving an initial 5-*exo*-*dig* attack of an ether at its gold π-alkyne to generate a carbocation-like intermediate **II**, eventually giving 3-alkoxy-1*H*-indene **2** or 1-indanone products (Scheme 1).[4a] For these 2-alkynylbenzyl ethers, we are aware of no instance to control the regioselective carboalkoxylation of their terminal alkyne analogues **3** to form 1- or 2-indanones selectively. Such 1- and 2-indanones are important structural motifs in several naturally occurring compounds; representatives include pterosin P,[5a–c] monachosorin A,[5a–c] (+)-pauciflorol F,[5d,e] taiwaniaquinol B,[5f] gloeophyllol C[5g] and caulerpal B[5h] that are depicted in Scheme 2. The chemoselective formation of the two indanones from the same 2-alkynylbenzyl ethers is highly de-




**Scheme 1.** Chemoselectivities for carboalkoxylations.

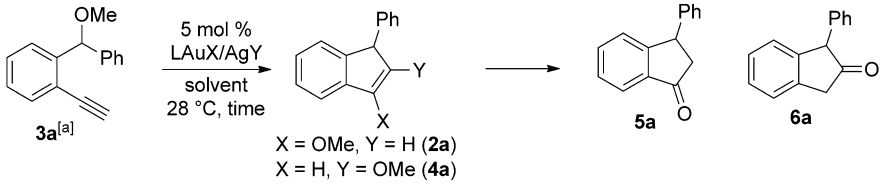



**Scheme 2.** Natural products bearing a 1- or 2-indanone moiety.

sired. The synthesis of 2-indanones is challenging because Au- and Pt-catalyzed carboalkoxylations of other terminal alkynes proceed preferably *via* 5-*exo-dig* rather than 6-*endo-dig* cyclizations.[2h,4b] Herein, we report chemoselective syntheses of 1- and 2-indanones with most ether substrates **3**, as optimized by gold catalysts and reaction solvents. The electron-rich gold catalyst P(*t*-Bu)$_2$(*ortho*-biphenyl)AuNTf$_2$ tends to favor 2-indanone derivatives in toluene (or dichloroethane) whereas the electron-deficient P(C$_6$F$_5$)$_3$AuSbF$_6$ produces preferably 1-indanone products in MeNO$_2$.

Shown in Table 1 is the control of the regioselectivity modulated by electron-deficient and electron-rich gold catalysts, respectively. We first tested P(*p*-CF$_3$C$_6$H$_4$)$_3$AuCl/AgSbF$_6$[4a] on terminal alkyne **3a** in dichloromethane (DCM), which yielded 1- and 2-indanones **5a** and **6a** in 48% and 37% yields, respectively; these indanones arose from a facile hydrolysis of their precursors **2a** and **4a** catalyzed with a gold catalyst. The chemoselectivity toward 1-indanone **5a** was significantly improved with acidic P(OPh)$_3$AuCl/AgSbF$_6$ and P(C$_6$F$_5$)$_3$AuCl/AgSbF$_6$, affording the desired **5a** in 70–72% yields, together with 2-indanone **6a** in minor proportions (13–15%). A polar solvent such as nitromethane enhanced the yield of 1-indanone **5a** to 87% if P(C$_6$F$_5$)$_3$AuCl/AgSbF$_6$ was used (entry 4). We then sought electron-rich gold catalysts to improve the chemoselectivity towards 2-indanone **6a**. P(*t*-Bu)$_2$(*o*-biphenyl)AuCl/AgX (X = SbF$_6$ and NTf$_2$) gave preferably 2-indanone **6a** in DCM with satisfactory yields (82–85%, entries 5 and 6). The

**Table 1.** Catalyst-dependent chemoselectivity.

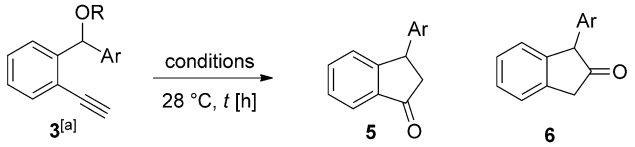



| Entry | L | Y | Solvent | Time [hour] | Yields [%][b] | |
|---|---|---|---|---|---|---|
| | | | | | **5a** | **6a** |
| 1 | P(*p*-CF$_3$C$_6$H$_4$)$_3$ | SbF$_6$ | DCM | 4 | 48 | 37 |
| 2 | P(OPh)$_3$ | SbF$_6$ | DCM | 4 | 70 | 13 |
| 3 | P(C$_6$F$_5$)$_3$ | SbF$_6$ | DCM | 2 | 72 | 15 |
| 4 | P(C$_6$F$_5$)$_3$ | SbF$_6$ | MeNO$_2$ | 4 | 87 | 8 |
| 5 | P(*t*-Bu)$_2$(*ortho*-biphenyl) | SbF$_6$ | DCM | 6 | 7 | 82 |
| 6 | P(*t*-Bu)$_2$(*ortho*-biphenyl) | NTf$_2$ | DCM | 6 | 5 | 85 |
| 7 | P(*t*-Bu)$_2$(*ortho*-biphenyl) | NTf$_2$ | DCE | 6 | trace | 92 |
| 8 | P(*t*-Bu)$_2$(*ortho*-biphenyl) | NTf$_2$ | toluene | 6 | trace | 82 |
| 9 | P(*t*-Bu)$_2$(*ortho*-biphenyl) | NTf$_2$ | MeNO$_2$ | 6 | 75 | 18 |
| 10 | IPr[c] | NTf$_2$ | DCM | 6 | 15 | 73 |

[a] [**3a**] = 0.1 M.
[b] Product yields are reported after purification from a silica column.
[c] IPr = 1,3-bis(diisopropylphenyl)imidazol-2-ylidene.

**Table 2.** Chemoselectivity over alkoxy and aryl substituents.




| Entry | Substrates | | | Conditions A[b] | | | Conditions B[b] | | |
|---|---|---|---|---|---|---|---|---|---|
| | **3** | R | Ar | *t* [h] | Yields [%][c] | | *t* [h] | **5** [%] | **6** [%] |
| 1 | **3b** | Et | Ph | 6 | **5a** (70) | **6a** (10) | 8 | **5a** (0) | **6a** (85) |
| 2 | **3c** | *n*-butyl | Ph | 6 | **5a** (77) | **6a** (18) | 8 | **5a** (0) | **6a** (76) |
| 3 | **3d** | allyl | Ph | 24[d] | – | – | 8 | **5a** (0) | **6a** (88) |
| 4 | **3e** | benzyl | Ph | 8 | **5a** (64) | **6a** (21) | 8 | **5a** (0) | **6a** (83) |
| 5 | **3f** | Me | 4-$MeC_6H_4$ | 4 | **5f** (83) | **6f** (0) | 6 | **5f** (0) | **6f** (92) |
| 6 | **3g** | Me | 4-$MeOC_6H_4$ | 4 | **5g** (84) | **6g** (0) | 10 | **5g** (79) | **6g** (0) |
| 7 | **3h** | Me | 4-$ClC_6H_4$ | 4 | **5h** (72) | **6h** (0) | 10 | **5h** (0) | **6h** (73) |
| 8 | **3i** | Me | 4-$FC_6H_4$ | 4 | **5i** (78) | **6i** (12) | 6 | **5i** (0) | **6i** (88) |

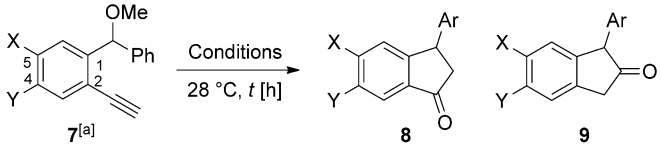
[a] [**3**] = 0.1 M, 5 mol% catalyst.
[b] Conditions **A**: $P(C_6F_5)_3AuSbF_6/MeNO_2$; conditions **B**: P(*t*-Bu)$_2$(*ortho*-biphenyl)$AuNTf_2$/DCE.
[c] Product yields are reported after separation on a silica column.
[d] Starting **3d** was recovered in 76%.

same reactions in dichloroethane (DCE) and toluene produced 2-indanone exclusively (82–92%, entries 7 and 8). Surprisingly, use of nitromethane reversed the chemoselectivity to afford mainly 1-indanone **5a** in 75% yield (entry 9). IPrAuCl/$AgNTf_2$ [IPr = 1,3-bis-(diisopropylphenyl)imidazol-2-ylidene] in DCM gave 1- and 2-indanones **5a** and **6a** in 15% and 73% yields, respectively (entry 10).

Inspired by these preliminary results, we prepared benzyl ethers **3b–3i** to assess their substituent effects. We examined the catalyst-dependent chemoselectivity, using $P(C_6F_5)_3AuCl/AgSbF_6$ in $MeNO_2$ (conditions A), and P(*t*-Bu)$_2$(*ortho*-biphenyl)AuCl/$AgNTf_2$ in DCE (conditions B). As shown in Table 2, variable alkoxy groups as in ether substrates **3b–3e** (R = ethyl, *n*-butyl, allyl, benzyl) showed distinguishable chemoselectivity such that $P(C_6F_5)_3AuSbF_6$ gave 1-indanone **5a** as major species (64–77%, entries 1, 2 and 4) whereas P(*t*-Bu)$_2$(o-biphenyl)$NTf_2$ afforded 2-indanone **6a** exclusively (>76%). In entry 3, no reaction occurred for alloxy derivative **3d** with $P(C_6F_5)_3AuSbF_6$. An electron-rich 4-methylphenyl group as in benzyl ether **3f** was amenable to such a catalyst-dependent chemoselectivity to give 1- and 2-indanones **5f** and **6f** in 83% and 92% yields, respectively (entry 5). Nevertheless, 4-methoxyphenyl derivative **3g** gave only 1-indanone **5g** with 79–84% yields using the two catalysts (entry 6). For 4-chloro- and 4-fluorophenyl derivatives **3h** and **3i**, we again observed a distinct chemoselectivity with the two catalysts, affording indanones **5h**, **5i** and **6h**, **6i**, respectively, in 72–78% and 73–88% yields (entries 7 and 8). Most benzyl ethers in Table 2 gave 1- or 2-indanones **5** and **6** selectively with satisfactory yields (>60%). 4-Methoxyphenyl derivative **3g** (entry 6) represents an exception to form 1-indanone **5g** exclusively with the two catalysts; this methoxy group tends to stabilize the benzyl cation **II**, as depicted in Scheme 1.

Table 3 shows the effects of the benzene subsituents (X, Y) for benzyl ethers **7a–7k**. For an electron-withdrawing group as in ethers **7a–7c** (X = F, Cl, Br), $P(C_6F_5)_3AuSbF_6$ gave the desired 1-indanones **8a–8c** in 33–71% yields, together with 2-indanones **9a–9c** in 3–60% yields; in contrast, P(*t*-Bu)$_2$(*ortho*-biphenyl)-$AuNTf_2$ gave 2-indanones exclusively in 70–89% yields (entries 1–3). With the same substituents in the phenyl C-4 position (Y = F, Cl, Br), $P(C_6F_5)_3AuSbF_6$, gave only the expected 1-indanones **8d–8f** in 82–87% yields whereas P(*t*-Bu)$_2$(*ortho*-biphenyl)$AuNTf_2$ afforded 2-indanones **9d–9f** in 73–84% yields (entries 4–6). Such a catalyst-dependent selectivity was applicable to benzyl ethers **7g–7i** bearing an alkyl group (X = Me, Y = H; X = H, Y = Me, *t*-Bu); the respective 1-indanones **8g–8i** and 2-indanones **9g–9i** were produced selectively with satisfactory yields (> 73%, entries 7–9). For benzyl ether **7j** bearing a methoxy at the phenyl C-5 position, both catalysts gave a mixture of 1- and 2-indanones **8j** and **9j** in significant portions (entry 10). For ether **7k** bearing a C-4 methoxy group (entry 11), $P(C_6F_5)_3AuSbF_6$ gave only 1-indanone **8k** in 87% yield, whereas P(*t*-Bu)$_2$(*ortho*-biphenyl)$AuNTf_2$ delivered 1- and 2-indanones **8k** and **9k** in comparable yields (36–39%). With P(*t*-Bu)$_2$(*ortho*-biphenyl)$AuNTf_2$, the majority of the benzyl ethers **7** in Table 3 gave 2-indanones **9a–9i** as the sole or major products; species **7k** represented an exception because its C-4 substituted methoxy group favored the formation of a benzyl cation **II** as depicted in Scheme 1. With $P(C_6F_5)AuSbF_6$, 1-indanone products **8** were obtained efficiently for most benzyl

**Table 3.** Substituent effects of the bridging benzenes.



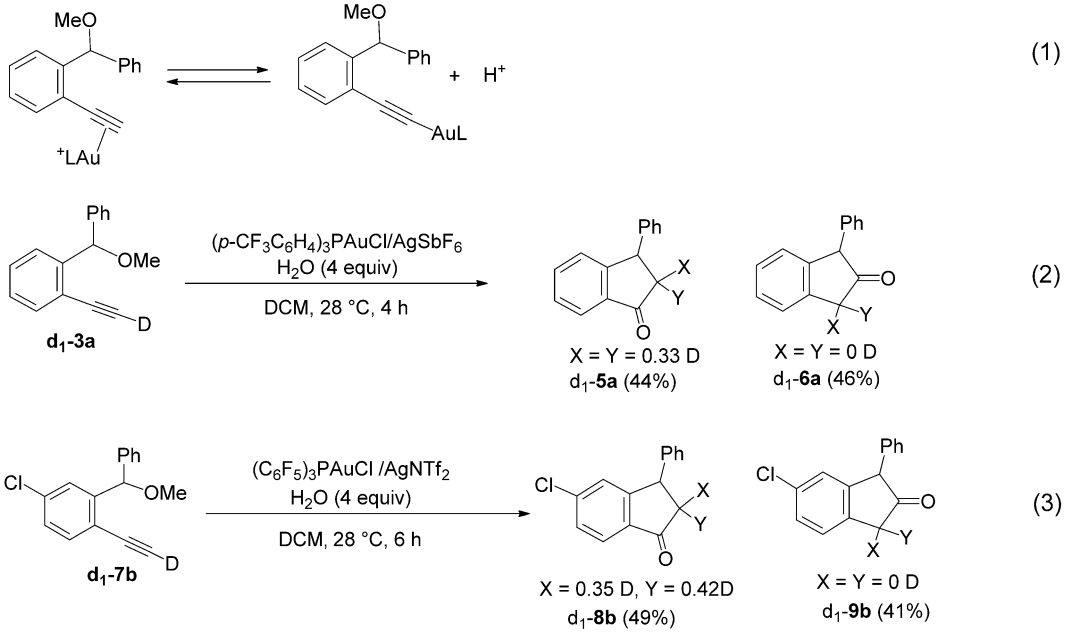

7[a] 8 9

| Entry | Substrates | | | Conditions A[b] | | | Conditions B[b] | | |
|---|---|---|---|---|---|---|---|---|---|
| | **7** | X | Y | *t* [h] | Yields [%][c] | | *t* [h] | Yields [%][c] | |
| 1 | **7a** | F | H | 5 | **8a** (48) | **9a** (42) | 8 | **8a** (0) | **9a** (70) |
| 2 | **7b** | Cl | H | 6 | **8b** (33) | **9b** (60) | 8 | **8b** (0) | **9b** (89) |
| 3 | **7c** | Br | H | 5 | **8c** (71) | **9c** (3) | 8 | **8c** (0) | **9c** (80) |
| 4 | **7d** | H | F | 5 | **8d** (82) | **9d** (0) | 8 | **8d** (0) | **9d** (84) |
| 5 | **7e** | H | Cl | 5 | **8e** (87) | **9e** (0) | 10 | **8e** (0) | **9e** (79) |
| 6 | **7f** | H | Br | 4 | **8f** (86) | **9f** (0) | 10 | **8f** (0) | **9f** (73) |
| 7 | **7g** | Me | H | 5 | **8g** (85) | **9g** (0) | 8 | **8g** (0) | **9g** (82) |
| 8 | **7h** | H | Me | 4 | **8h** (92) | **9h** (0) | 10 | **8h** (0) | **9h** (73) |
| 9 | **7i** | H | *t*-Bu | 4 | **8i** (82) | **9i** (0) | 5 | **8i** (0) | **9i** (90) |
| 10 | **7j** | OMe | H | 4 | **8j** (27) | **9j** (33) | 10 | **8j** (20) | **9j** (60) |
| 11 | **7k** | H | OMe | 4 | **8k** (87) | **9k** (0) | 5 | **8k** (36) | **9k** (39) |

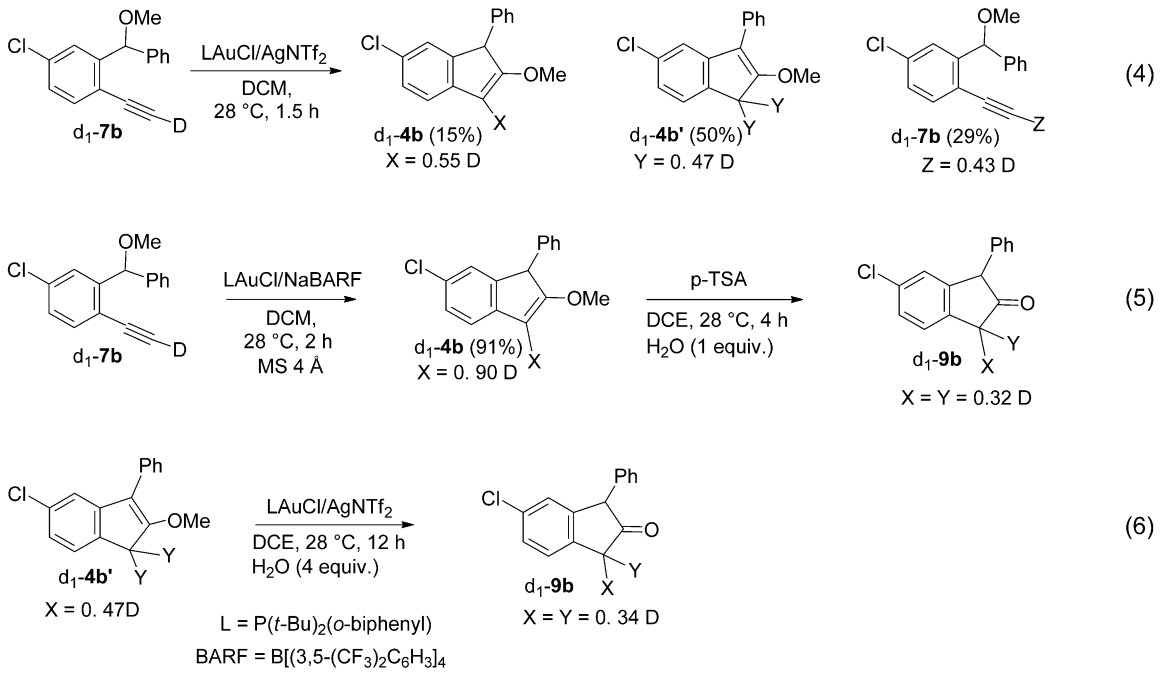
[a] [**7**] = 0.1 M, 5 mol% catalyst.
[b] Conditions **A**: $P(C_6F_5)_3AuSbF_6/MeNO_2$; conditions **B**: $P(t\text{-Bu})_2$(*ortho*-biphenyl)$AuNTf_2$/DCE.
[c] Product yields are reported after separation on a silica column.

ethers **7** except for those bearing X = F, Cl and OMe (entries 1, 2 and 10).

Electron-rich gold complexes react with acidic terminal alkynes to form alkynylgold complexes reversibly [Eq. (1)],[6,7] the roles of π-alkynes and alkynylgold species in the reaction chemoselectivity are unclear. We performed deuterium labeling experiments using $P(4\text{-}CF_3C_6H_4)_3AuSbF_6$ on benzyl ether $d_1$-**3a**, affording 1- and 2-indanones **5a** and **6a** in comparable proportions [44–46% yields, Eq. (2)]. In the presence of added water (4 equiv.) in DCM, 1-indanone $d_1$-**5a** retained 66% deuterium content whereas $d_1$-**6a** completely lost deuterium. A small loss of deuterium content for $d_1$-**5a** is due to an equilibrium between π-alkyne and alkynylgold species [Eq. (1)].[6,7] We tested the reaction of $d_1$-**7b** with $(C_6F_5)_3PAuCl/AgNTf_2$ in wet DCE (4.0 equiv. $H_2O$), giving 1-indanone ($d_1$-**8b**) and 2-indanone ($d_1$-**9a**) comprising 84% and 0% deuterium contents. This information leads us to postulate that 1-indanones are generated from π-alkyne species because of the small deuterium loss, even though water is present in a large proportion





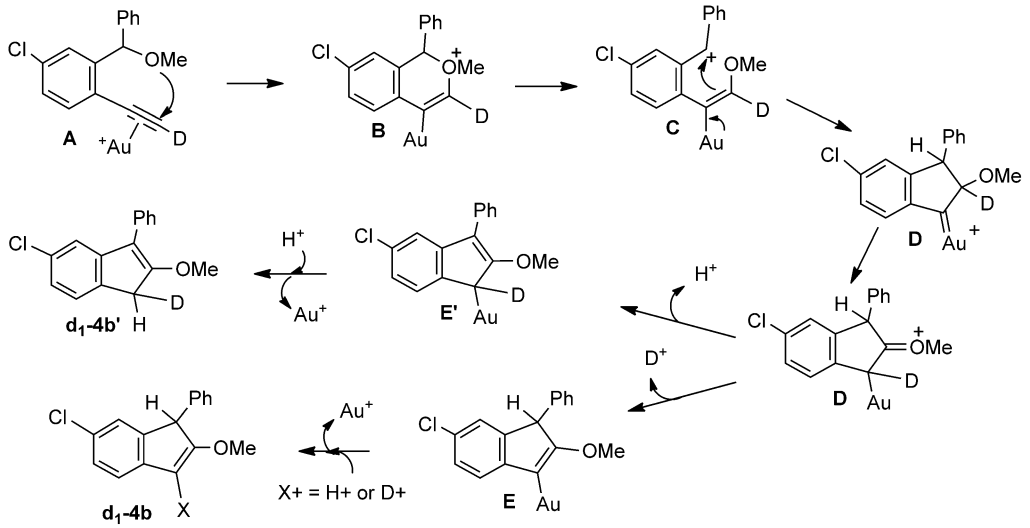

(4 equiv); the mechanism is essentially the same as that postulated by Toste (Scheme 1).

In the carboalkoxylation of terminal alkynes, a tethered ether typically attacks the alkyne C-2 carbon, as exemplified by 1-indanone products.[2h,3c,d,4] The formation of 2-indanones **6** and **9** from benzyl ethers **3** and **7** remains mechanistically unclear. We attempted to isolate their enol ether precursors to seek the solution. As shown in Eq. (4), a brief reaction (1.5 h) between deuterated $d_1$-**7b** and P(*t*-Bu)$_2$(*ortho*-biphenyl)-AuNTf$_2$ (5 mol%) in freshly distilled DCM (28 °C, 1.5 h) led to a 70% conversion, from which two indenyl methyl ethers $d_1$-**4b** and $d_1$-**4b′** were isolated in 15% and 50% yields, together with unreacted $d_1$-**7b** in 29% recovery. $^1$H NMR analysis revealed that major enol ether $d_1$-**4b′** contained 94% deuterium content (Y = 0.47 D) whereas minor ether $d_1$-**4b** had 55% deuterium content (X = 0.55 D), slightly higher than that (Z = 0.43 D) of unreacted $d_1$-**7b**. With P(*t*-Bu)$_2$(*ortho*-biphenyl)AuBARF {BARF = B[3,5-(CF$_3$)$_2$C$_6$H$_3$]$_4$} in dry DCM (28 °C, MS 4 Å, 2 h), species $d_1$-**7a** provided only enol ether $d_1$-**4b** containing 90% deuterium contents [X = 0.90 D, Eq. (5)]. Notably, enol ethers $d_1$-**4b** and $d_1$-**4b′** underwent no interconversion to each other in the presence of P(*t*-Bu)$_2$(*ortho*-biphenyl)NTf$_2$ in freshly distilled DCM (28 °C, 4 h), in which we observed no deuterium loss for both $d_1$-**4b** and $d_1$-**4b′**.[8] The two ethers remained intact upon treatment with P(*t*-Bu)$_2$(*ortho*-biphenyl)NTf$_2$ in wet DCE (28 °C, 12 h) because no Brønsted acid was present in this system.[8] Treatment of enol ethers $d_1$-**4b** and $d_1$-**4b′** with *p*-TSA (10 mol%) in wet DCE (4 equiv. H$_2$O) led to 2-indanone **9b** with *ca.* 30% deuterium loss [eqs. (5) and (6)].[9]

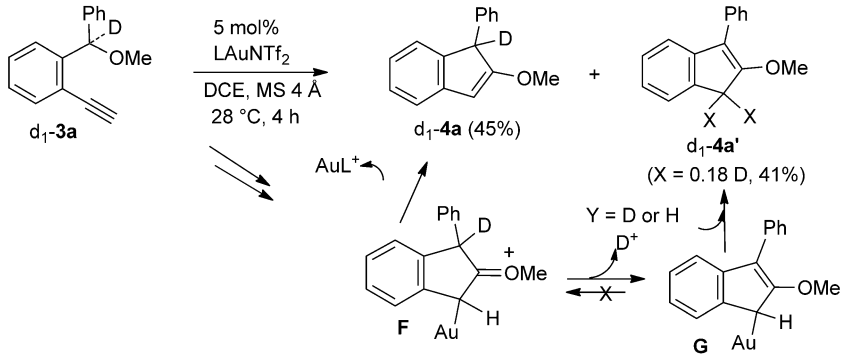
The deuterium experiment in Eq. (4) suggests the intermediacy of gold π-alkynes to form 2-indanone products. Alkynylgold species in Eq. (1) enable a complete exchange between the alkynyl proton of initial $d_1$-**7b** and H$_2$O.[6,7] To balance the deuterium mass of species $d_1$-**4a**, $d_1$-**4a′** and unreacted $d_1$-**7b** in Eq. (4), external H$_2$O with 0.16 equiv. provided the proton source. Hence, the alkynylgold activation is expected to give indenyl methyl ethers **4a** and **4a′** with deuterium contents of less than 68%, but the resulting major ether **4a′** has a large deuterium content of *ca.* 94%. Accordingly, we postulate a *6-endo-dig* cyclization for the initial π-alkyne species **A** to form the oxonium-like species **B**, subsequently producing benzyl cation **C** (Scheme 3). An intramolecular cyclization of this benzyl cation is expected to give gold carbenes **D** that undergo a complete 1,2-deuterium shift.[10] To rationalize the different deuterium contents of ethers **4b** and **4b′** [Eq. (4)], we envisage that the two non-aromatic protons of species **D** are sufficiently acidic to cause its dissociation, giving gold containing enol ethers **E** and **E′**, respectively. Subsequent protodeaurations of species **E** and **E′** afford indenyl methyl ethers **E** and **E′**; the former loses significant deuterium content whereas species **E′** retains the same deuterium content.

The proposed mechanism is based on deuterium analyses of two isolable indenyl methyl ethers **4b** and **4b′** [eq. (4)]; we devised another experiment to support this mechanism (Scheme 4). We prepared $d_1$-**3a** bearing a benzylic deuterium; its gold-catalyzed car-




**Scheme 3.** A π-alkyne route to 2-indanones.



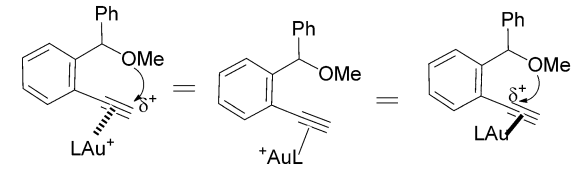

**Scheme 4.** Additional labeling experiment.

boalkoxylation in dry DCE (28 °C, MS 4 Å) also afforded two indenyl methyl ethers **4a** and **4a′** in 45% and 41% yields, respectively. Enol ether $d_1$-**4a** was fully deuterated at its benzylic position, indicating that the key **F**→**G** transformation was irreversible because of a facile deauration step **F**→$d_1$-**4a**. The other enol ether $d_1$-**4a′** had only 36% deuterium content (X = 0.18 D), indicative of a protodeauration of species **G** with an external proton source. In contrast with transformation **D**→$d_1$-**4b** (Scheme 2), we postulated a direct deauration for transformation **F**→$d_1$-**4a** because the olefin moiety of $d_1$-**4a** contained no deuterium that would be expected to be present in solution in a small proportion. Without a chloro substituent, we envisage that the Au–C–H proton of species **F** is insufficiently acidic to induce a dissociation of the proton.

Most of the 2-alkynylbenzyl ethers can deliver 1- and 2-indanone products using $P(C_6F_5)_3AuSbF_6$ and P(*t*-Bu)$_2$(*ortho*-biphenyl)AuNTf$_2$, in $MeNO_2$ and DCE respectively. The mechanism of 2-indanones involves a 6-*endo-dig* cyclization rather than a typical 5-*exo-dig* cyclization.[2h,3c,d,4] Our rationalization on the catalyst-dependent selectivity is highly speculative; we envisage that the strongly acidic gold complex $P(C_6F_5)_3AuSbF_6$ generates a new positive charge on the π-alkyne C-2 carbon that can be stabilized by the neighboring benzene group. For the less acidic P(*t*-Bu)$_2$(*ortho*-biphenyl)AuNTf$_2$, the charge distribution of the π-alkyne is affected by the intrinsic property of the alkyne itself, in which the C-1 carbon is more electron-deficient than the C-2 carbon if benzene is considered to be a withdrawing group. Accordingly, this C-1 regioselectivity is particularly favored by an electron-deficient benzene, compatible with our observation (Table 2, entries 1 and 2). We remain uncertain about the reason for the solvent effects that significantly affect the chemoselectivity.

In this work, we have reported selective syntheses of 1- and 2-indanones from most 2-ethynylbenzyl ethers optimized with gold catalysts and solvents. Highly acidic $P(C_6F_5)_3AuSbF_6$ in $MeNO_2$ preferably gives 1-indanones whereas electron-rich P(*t*-Bu)$_2$(*ortho*-biphenyl)AuNTf$_2$ in DCE tends to form 2-




L = P(*t*-Bu)$_2$(*o*-biphenyl) L = P(C$_6$F$_5$)$_3$

indanones. For 2-indanone products, our mechanistic studies support a π-alkyne activation; herein, we isolated two enol ether species for deuterium labeling analyses.[12] These results reveal the feasibility of a 6-*endo-dig* cyclization of terminal alkynes that can be dominant over a 5-*exo-dig* mode when electron-rich gold catalysts were employed in suitable solvents

## Experimental Section

### General Procedure for Synthesis of 3-Phenyl-2,3-dihydro-1*H*-inden-1-one (5a)

To a wet nitromethane solution (2.5 mL) of ClAuP(C$_6$F$_5$)$_3$ (13.8 mg, 5 mol%) and AgSbF$_6$ (6.0 mg, 5 mol%) was added a nitromethane solution (1 mL) of 1-ethynyl-2-(methoxy-(phenyl)methyl)benzene (**3a**, 78 mg, 0.35 mmol) at 28 °C. The reaction mixture was stirred for 4 h before it was concentrated and eluted through a silica column to afford compound **5a** (yield: 63 mg, 87%) and compound **6a** (yield: 6 mg, 8%) as a colorless oil. IR (neat): ν = 3086 (w), 1672 (s), 1533 cm$^{-1}$ (m); $^1$H NMR (400 MHz, CDCl$_3$): δ = 7.81 (d, *J* = 7.6 Hz, 1H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.33 ~ 7.22 (m, 4H), 7.12 (d, *J* = 7.2 Hz, 2H), 4.57 (dd, *J* = 8.0, 3.6 Hz, 1H), 3.22 (dd, *J* = 19.2, 8.0 Hz, 1H), 2.68 (dd, *J* = 19.2, 4.0 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ = 206.0, 157.9, 143.6, 136.7, 125.1, 128.9, 127.8, 127.6, 127.0, 126.8, 123.4, 46.8, 44.4; HR-MS: *m/z* = 208.0884, calcd. for C$_{15}$H$_{12}$O: 208.0888.

### General Procedure for Synthesis of 1-Phenyl-1*H*-inden-2(3*H*)-one (6a)

To a wet 1,2-dichloroethane solution 2.5 (mL) of ClAuP(*t*-Bu)$_2$(*ortho*-biphenyl) (9.3 mg, 5 mol%) and AgNTf$_2$ (6.8 mg, 5 mol%) was added a 1,2-dichloroethane solution (1 mL) of 1-ethynyl-2-[methoxy(phenyl)methyl]benzene (**3a**, 78 mg, 0.35 mmol) at 28 °C. The reaction mixture was stirred for 6 h before it was concentrated and eluted through a silica column to afford compound **6a** as colorless oil; yield: 67 mg (92%). IR (neat): ν = 3084 (w), 1768 (s), 1542 cm$^{-1}$ (m); $^1$H NMR (400 MHz, CDCl$_3$): δ = 7.39 ~ 7.25 (m, 6H), 7.18 (d, *J* = 7.2 Hz, 1H), 7.10 (d, *J* = 8.4 Hz, 2H), 4.67 (s, 1H), 3.66 (s, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ = 213.9, 141.3, 138.1, 137.2, 128.8, 128.4, 128.0, 127.8, 127.3, 126.0, 124.8, 59.7, 43.0; HR-MS: *m/z* = 208.0887, calcd. for C$_{15}$H$_{12}$O: 208.0888.

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[8] In catalytic carboalkoxylations, we envisage that the Brønsted acid is generated from the π-alkyne/σ-acetylide equilibrium to facilitate the hydrolysis of enol ethers **4b** and **4b′**. To test this hypothesis, $d_1$-**4b** was treated with P(*t*-Bu)$_2$(*ortho*-biphenyl)AgNTf$_2$ and phenylacetylene (20 mol%) in wet DCE, giving 2-indanone product $d_1$-**9b** with 70% deuterium content (X = Y = 0.35 D). No deuterium loss was observed for recovered $d_1$-**4b**. We observed a similar phenomenon for the other enol ether $d_1$-**4b′**.

[9] A partial loss of deuterium contents of 2-indanone $d_1$-**9b** from starting $d_1$-**4b** and $d_1$-**4b′** [Eqs. (5) and (6)] indicates that two equilibrium states ($d_1$-**4b**/**F** and $d_1$-**4b′**/**F**) likely occur before 2-indanone **9b** is produced. This phenomenon reveals a risk of obtaining low enantioselectivity in the carboalkoxylation of 2-ethynylbenzyl ethers with chiral gold catalysts. In contrast, 1-indanone products avoid this process; see ref.[4b]

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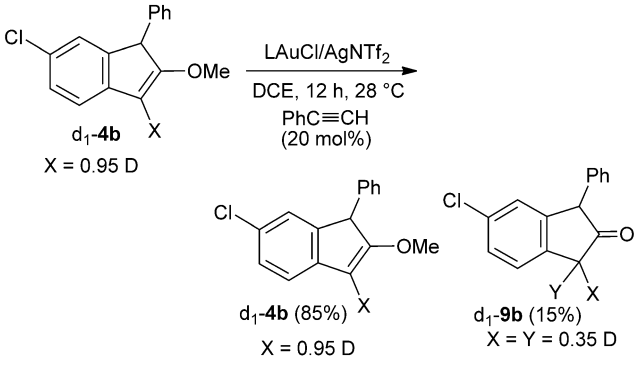
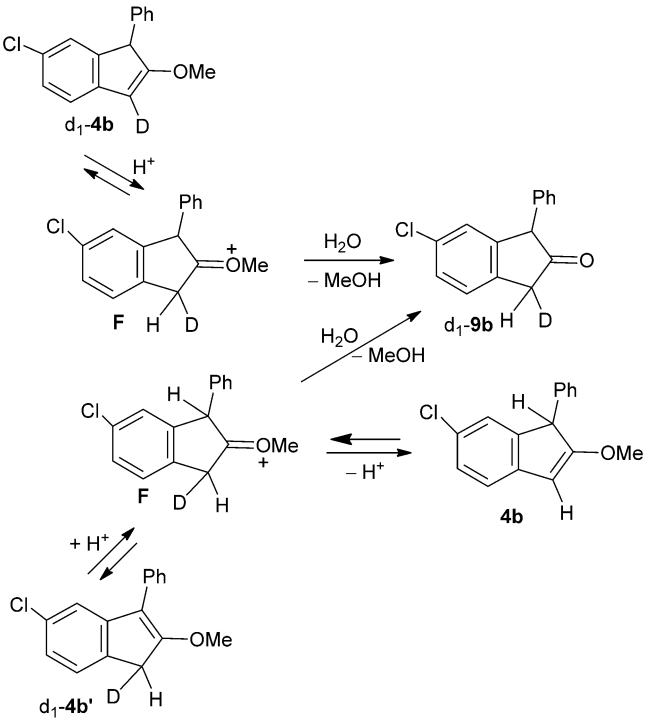
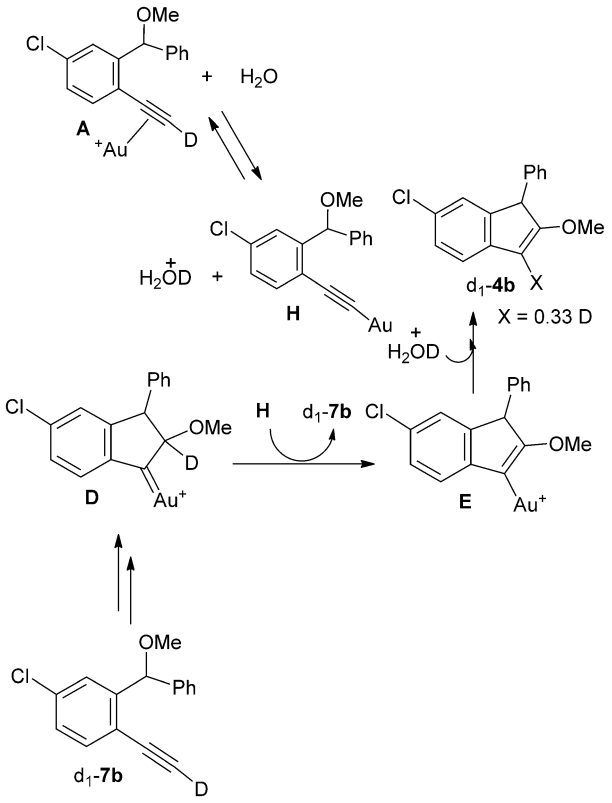
[12] A large deuterium loss of $d_1$-**6a** and $d_1$-**9b** [Eqs. (2) and 3] is not due to the proton exchange of 2-indanone products with water in the presence of gold catalyst. Partial deuterium loss was observed for formation of enol ether $d_1$-**4b** [Eq. (4)]0, and also for the hydrolysis of two enol ethers $d_1$-**4b** and $d_1$-**4b′** [Eqs. (5) and (6) and ref.[9]]. We do not rule out the possibility that water[13] increases the concentration of alkynylgold species **H** to assist the proton dissociation of key inter-






mediate **D**, thus resulting in a large deuterium loss for resulting enol ether $d_1$-**4b**.

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