PPh_3AuTFA catalyzed dearomatization of 2-naphthols with allenamides

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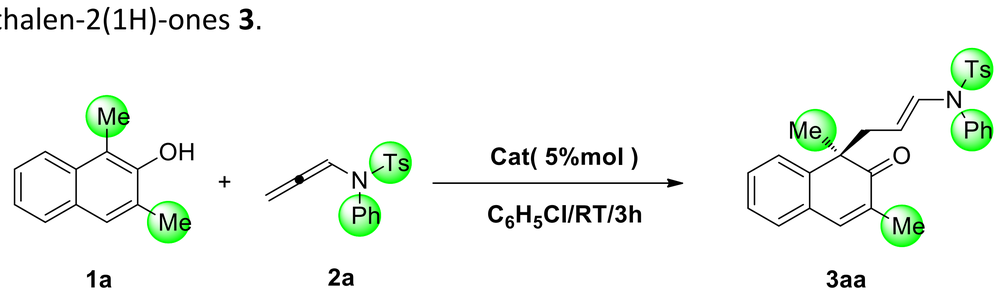
Aromatic compounds are readly availabe and cheap building blocks to obtain pharmaceuticals and biologically active species. Over the past decade, dearomatization of arenes is receiving an explosive research enthusiasm among synthetic chemists. [1]

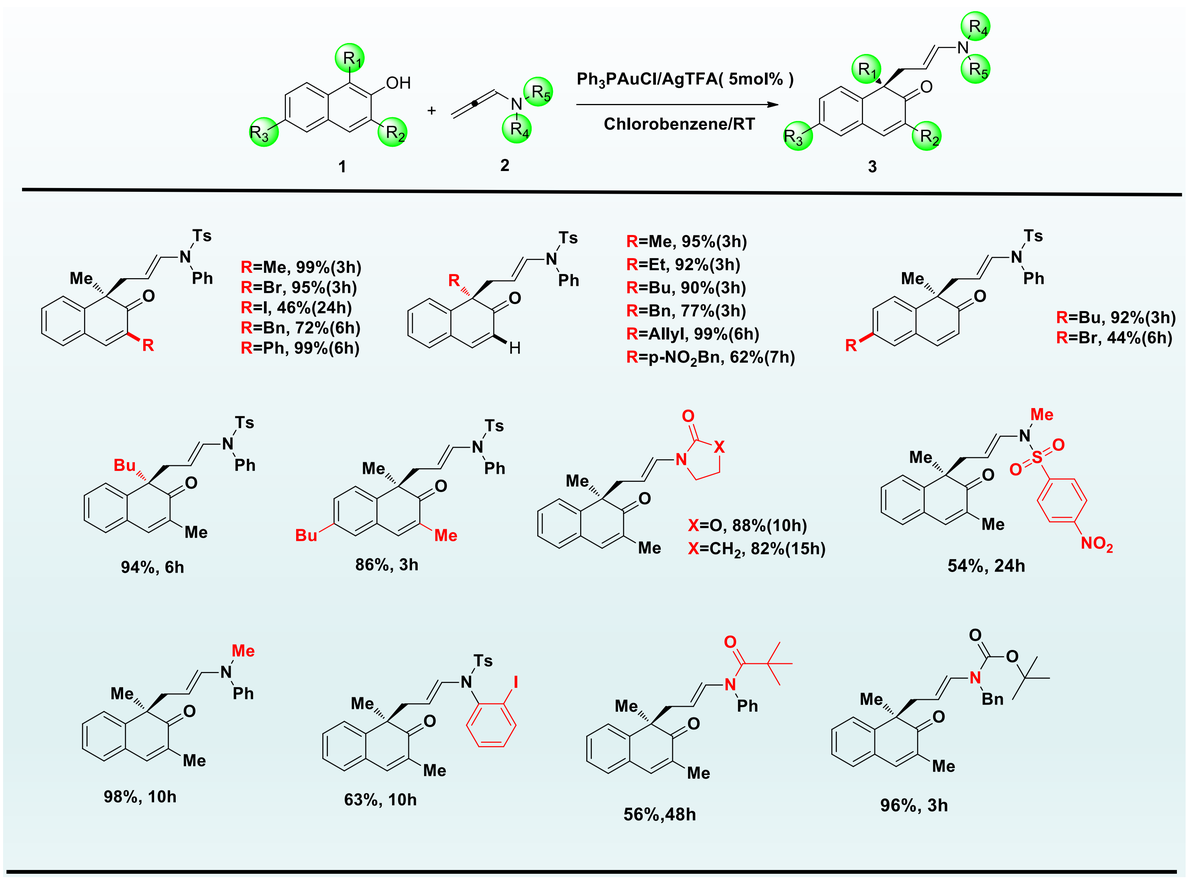
In conjunction with our interests on the catalytic manipulation of arenes and heteroarenes,[2,3] we present here an unprecedented gold-catalyzed intermolecular dearomatization protocol of 2-naphthols with *N*-allenyl amides to give C(1)-allylated naphthalen-2(1H)-ones **3**.



Run	Cat	Yield 3aa (%)[a]
1	Ph_3PAuCl/AgTFA	98
2	Ph_3PAuCl/AgOTf	decomposition[b]
3	Ph_3PAuCl/AgOTs	10
4	Ph_3PAuCl/AgOAc	traces
5	Ph_3PAuCl/$AgNTf_2$	decomposition[b]
6	JohnPhosAuCl/AgTFA	66
7	IPrAuCl/AgTFA	55
8	$picAuCl_2$/AgTFA[c]	71
9	without AgTFA	NR
10	without PPh_3AuCl	29
11	PPh_3AuTFA[d]	92

Table 1: a): Determined after flash chromatography. b): Referred to **2a**. c): With AgTFA (10 mol%). d):Preformed complex was employed. NR: no reaction. In all cases only the (*E*)-**3aa** was isolated.

To explore the intrinsic attitude of [Au(I)] species in performing specific electrophilic activation of allenes, we firstly screened several reaction conditions (Table 1) by obtaining the optimal parameters listed in the entry 1.

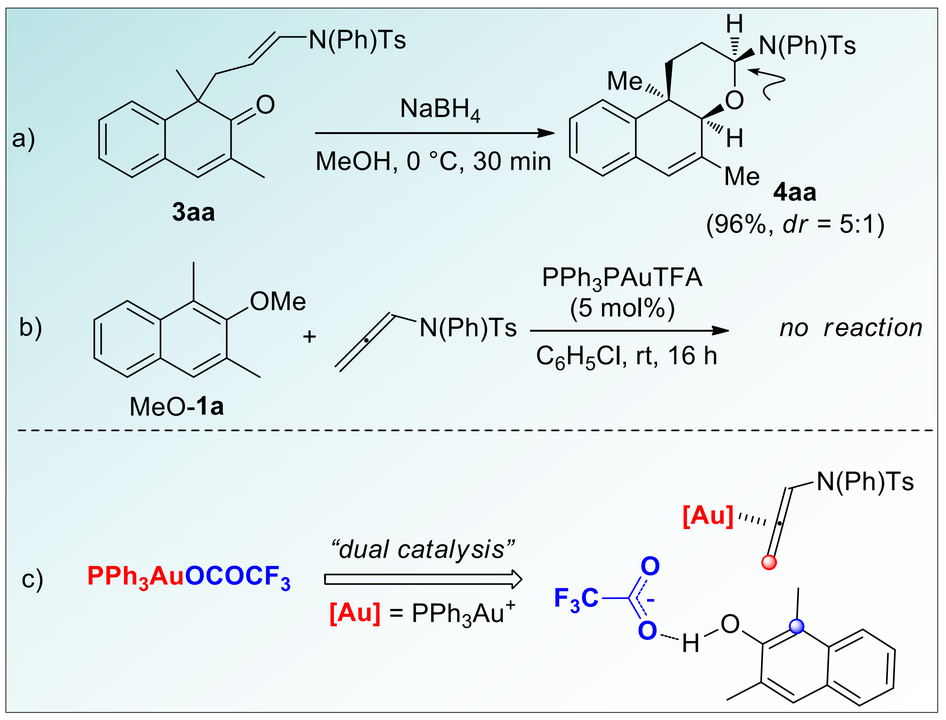


Scheme 1. Proving the substrate scope.

With the optimized conditions, we then focused on the scope of substrates (Scheme 1). We have screened various substrates including electron-withdrawing group, electron-donating group at different positions of naphthol and we also studied the influence of a series of allenamides. In all cases, high levels of chemoselectivity and stereoselectivity were obtained along excellent yields (up to 98%).

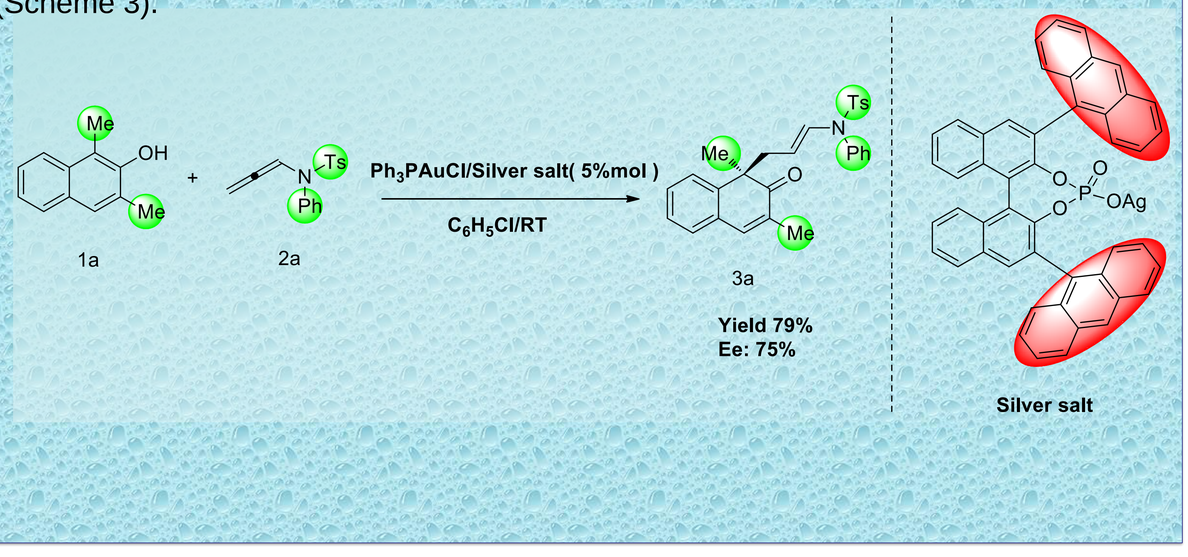
After expanding substrates scope, application of polycyclic C(1)-allylated naphthalen-2(1H)-ones was proceeded (Scheme 2, a). Surprisingly, under the assistance of $NaBH_4$, naphthalen-2(1H)-one experienced a cascade reaction to give the cyclized *1H*-benzochromene **4aa** in high yield (96%) and good diastereoisomeric control (5:1).

In addition, control experiment was also completed via protection of hydroxyl group of naphthol in model reaction conditions. From this result and NMR investigation a "dual-activation" mode played by the PPh_3AuTFA is postulated being active along the reaction mechanism.



Scheme 2

At last, we turned our attention to control the enantioselective profile of the methodology. Interestingly, promising results were obtained by means of the chiral counteranion approach based on phosphoric silver salts).[4] Er up to 88:12 were obtained in the presence of 3,3'-bis(9-anthracenyl) substituted binaphthyl scaffold (Scheme 3).



Scheme 3

Reference

[1] A. R. Pape, K.P. Kaliappan, E. P. Kündig, *Chem. Rev.* **2000**, *100*, 2917-2940.
[2] C. Romano, M. Jia, M. Monari, E. Manoni, M. Bandini, *Angew. Chem. Int. Ed.* **2014**, *53*, 13854-13857;
[3] M. Bandini, *Chem. Soc. Rev*. **2011**, *40*, 1358-1367.
[4] G. L. Hamilton, E. J.Kang, M. Mba, F. D. Toste, *Nature*, **2007**, *317*, 496-499.