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PPh3AuTFA “dual-catalysis” in the dearomatization of 2-naphthols with allenamides

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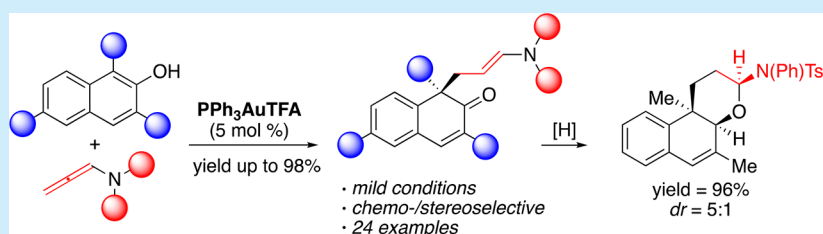
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PPh₃AuTFA Catalyzed in the Dearomatization of 2-Naphthols with Allenamides

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S Supporting Information



ABSTRACT: A new catalytic methodology for the direct dearomatization of substituted 2-naphthols via intermolecular condensation with allenamides is presented. PPh₃AuTFA (5 mol %) promotes the formal allylating dearomative protocol under mild conditions, large scope (24 examples), and high regioselectivity and stereoselectivity. The synergistic catalytic role played by the [PPh₃Au]⁺ (π -acid) and TFA⁻ (Lewis base) is highlighted.

The catalytic dearomatization of 2-naphthols represents a desirable synthetic shortcut to a structurally elaborated 3D-chemical space starting from readily accessible two-dimensional (2D) congeners.¹ The installation of a new stereogenic center at the C(1) position of the naphthyl core enables the realization of a number of key molecular motifs found in numerous bioactive and naturally occurring compounds (Figure 1, upper portion).²

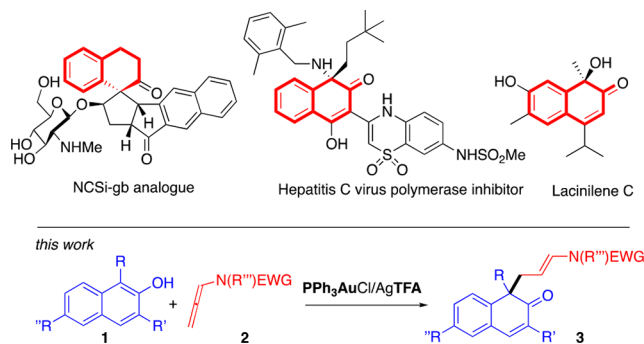


Figure 1. Examples of naturally occurring compounds comprising partially dearomatized naphthyl cores (upper panel). The present work representation of dearomatization protocols (lower panel).

Catalytic dearomatization of naphthols are generally categorized in oxidative and nonoxidative procedures. While in the former case, the formation of C–X (for X = O, N, halide) linkage is involved,³ the latter approach commonly involves the formation of new C–C connections with a desirable carbon-based decoration of the arene periphery.⁴ In the latter approach, the use of inexpensive and readily available unsaturated hydrocarbons deserve a peculiar mention, because

of the intrinsic atom economy and ready access to chemical complexity/diversity.⁵

In continuation with our ongoing interests in the metal as well as organocatalyzed dearomatization of electron-activated arene,⁶ we have recently documented the impact of the gold counterion⁷ on the overall chemochemical, regiochemical, and stereochemical outcome of the dearomatization of C2,3-disubstituted indoles with allenamides.^{8,9}

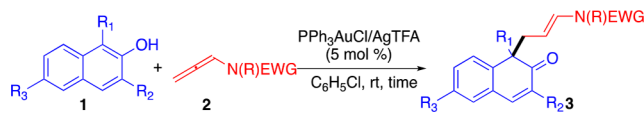
In particular, the use of trifluoroacetate (TFA) anion enabled the site-selective C(3)-allylic alkylation of N(H)-indoles with consequent dearomatization of the pyrrolyl ring.^{6b} The instauration of hydrogen-bond interactions between the indole and the anion was postulated and verified via nuclear magnetic resonance (NMR) analysis, providing a concrete rationale for the final regiochemical outcome.^{6c}

In the present work, we describe the implementation of this adaptive methodology to the C(1)-site-selective intermolecular dearomatization of 2-naphthols **1** with allenamides (**2**) to furnish formally C(1)-allylated naphthalen-2(1H)-ones (**3**).

Interestingly, the use of Ph₃PAuCl/AgTFA (5 mol %) governed the regioselective and stereoselective condensation of 1,3-(Me)₂-naphthyl-2-ol (**1a**) to allenamide **2a** in almost quantitative yield (98%, room temperature (rt), 3 h; see Table 1, entry 1). Deviations from the optimal conditions generally caused a drop in catalytic performance, as listed in Table 1.

In particular, chlorobenzene proved to be the solvent of election among those tested, providing the highest yield in short reaction times (3 h). To gain preliminary insight into the counterion role, a range of silver-based halide scavengers was assessed (Table 1, entries 6–10). Interestingly, while strongly

Table 1. Optimization of the Reaction Conditions^a



run	deviation from optimal	yield of 3aa ^b (%)
1	–	98
2	CH ₃ CN is used as the solvent	NR
3	toluene is used as the solvent	50
4	THF is used as the solvent	traces
5	CH ₂ Cl ₂ is used as the solvent	62
6	AgOTf	decomposition ^c
7	AgOTs	10
8	AgOAc	traces
9	AgOPNB ^d	traces
10	AgSbF ₆ ^e	decomposition ^c
11	AgNTf ₂	decomposition ^c
12	reagent-grade C ₆ H ₅ Cl	65
13	JohnPhosAuCl/AgTFA	66
14	IPrAuCl/AgTFA	55
15	picAuCl ₂ /AgTFA ^f	71
16	without AgTFA	NR ^g
17	without PPh ₃ AuCl	29
18	PPh ₃ AuTFA ^h	92

^aReaction conditions: **1a** (0.05 M). **1a**:**2a**:PPh₃AuCl:AgTFA = 1/2/0.05/0.05 under anhydrous conditions, unless otherwise specified. In all cases, only the (*E*)-**3aa** isomer was isolated. ^bDetermined after flash chromatography. ^cWith reference to **2a**. ^dOPNB = *p*-NO₂-benzoate. ^eReaction temperatures: 0 °C. ^fWith picAuCl (5 mol %) and AgTFA (10 mol %). ^gNR = no reaction. ^hPreformed complex was employed.

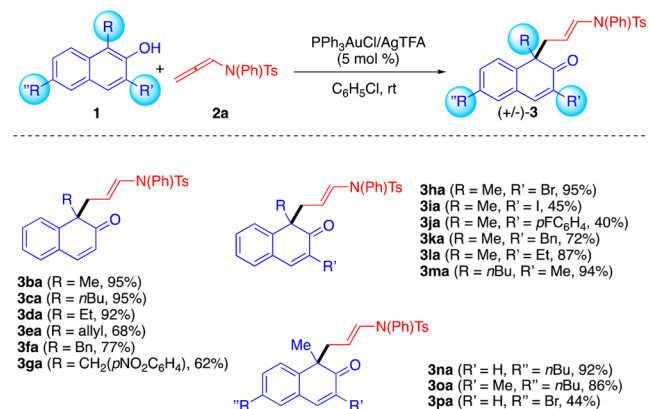
coordinating anions such as OTs[–] and AcO[–] did not promote the reaction in any extent (Table 1, entries 7 and 8), the employment of poorly coordinating analogous (i.e., SbF₆[–], OTf[–] and NTf₂[–]) caused complete decomposition of **2a**, even at lower temperatures.

Anhydrous conditions proved to be mandatory in order to achieve optimal yields (Table 1, entry 1 vs entry 12) and when different gold(I) or gold(III) sources were considered, a significant drop in chemical outcomes was recorded (Table 1, entries 13–15). We can categorize the present methodology as a silver-assisted-gold catalyzed methodology, since the simultaneous presence of both PPh₃AuCl and AgTFA worked far better than the single components alone (Table 1, entries 16 and 17). Finally, the efficiency of the preformed PPh₃AuTFA complex¹⁰ in performing the titled dearomatization was proven (yield = 92%, entry 18).¹¹

Having established desirable catalytic conditions, the scope of the protocol was initially assessed by considering a range of variously functionalized 2-naphthols with **2a**. The protocol proved tolerant toward substitutions at different positions of the naphthyl core (i.e., C(1), C(3), and C(6)) featuring complementary electronic as well as steric properties (yields = 40%–95%; see Scheme 1).

This aspect was particularly significant at the reactive site (i.e., C(1) carbon) where a range of alkyl groups (i.e., Me, Et, *n*Bu, allyl and Bn, **1b–1g**) was investigated. Aromatic and aliphatic atoms, as well as halogen atoms (i.e., bromo and iodo), were properly located at the C(3)-position (**1h–1m**) with satisfactory yields. In addition, analogous performance was recorded with substitutions at the C(6)-position (**1n–1p**).

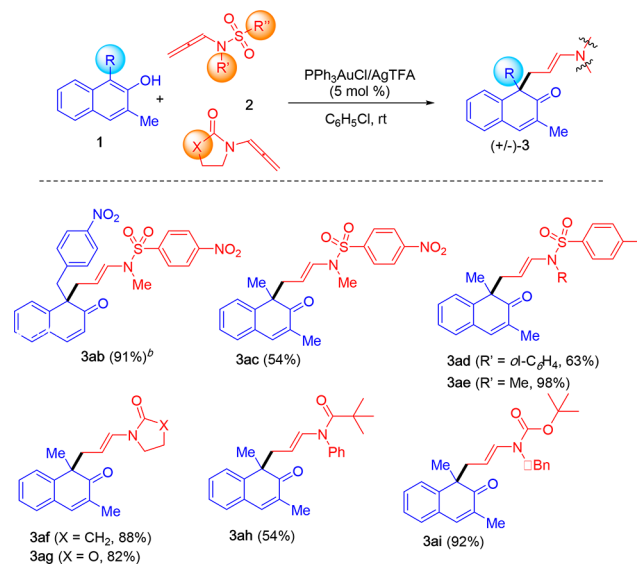
Scheme 1. Screening of Substituted Naphthols 1^a



^aReaction conditions: **1** (0.05 M) under anhydrous conditions (also see the Supporting Information (SI)).

Subsequently, a range of cyclic and acyclic allenamides (**2b–2h**) were subjected to the optimal conditions (Table 1, entry 1) and the corresponding results are summarized in Scheme 2.

Scheme 2. Screening of Substituted Allenamides 2^a

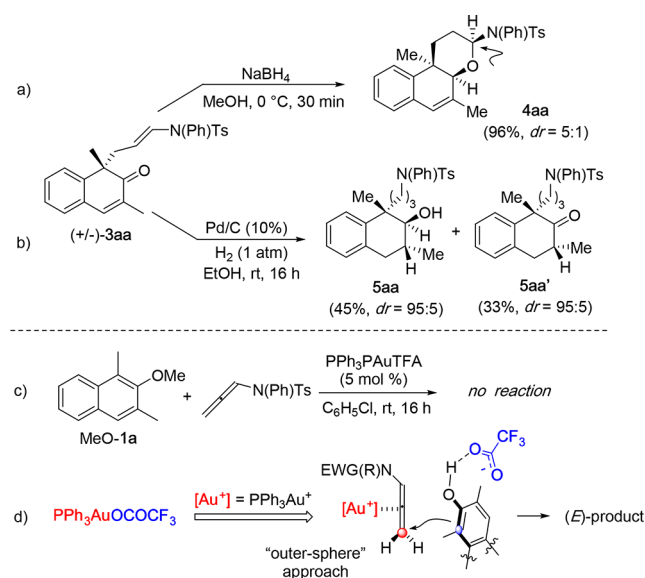


^aReaction conditions: **1** (0.05 M) under anhydrous conditions (also see the SI). ^b**1**:**2** = 1:3.

In all cases, the desired dearomatized naphthalen-2(1H)-one **3** was isolated in good to excellent yields (56%–96%) and high stereoselectivity in favor of the *E*-enamide moiety. However, the process faced also some limitations that were mostly related to the inertness of the α - and γ -substituted allenamides.¹²

The synthetic manipulation of the dearomatized adducts **3** was proven by subjecting compound **3aa** to the chemoselective reduction of the enone moiety with NaBH₄ in MeOH at room temperature (rt). Interestingly, the 1H-benzochromene **4aa** was isolated in high yield (96%) and good diastereomeric control (5:1) via concomitant trapping of the newly formed secondary alcohol by the enamide group (see Scheme 3a). In addition, the Pd/C (10 wt %, 10 mol %) catalyzed hydrogenation of **3aa** (H₂, 1 atm, EtOH, rt) was performed resulting in a separable 1.4:1 mixture of diastereomerically pure 1,2,3,4-

Scheme 3. Chemical Manipulation of the Dearomatized Naphthalenone Compounds **3** and Mechanism Proposal^a



^aThe outer-sphere approach was shown. Attempts to isolate the corresponding aldehyde via acidic hydrolysis of **3aa** were unfruitful, leading to the complete decomposition of the starting material.

tetrahydronaphthalene derivatives **5aa** and **5aa'** (see Scheme 3b).

Mechanistically, a synergistic π -acid/Lewis base catalysis is proposed for the observed outcome.¹³ In particular, beside the key electrophilic activation of the allenyl core¹⁴ exerted by the metal center,¹⁵ the simultaneous activating/directing action played by the “relatively” basic CF_3CO_2^- anion on the naphthol would guarantee the optimal electronic/spatial arrangement for the C–C bond forming process (see Scheme 3d; the outer-sphere-type approach is shown).^{5g,16} The pK_a of the corresponding conjugate acid (pK_a of TFAH ca. 0) can provide a rough indication of the desirable compromise among metal-coordination attitude and “hydrogen bond basicity”¹⁷ of the anionic species. In particular, while more coordinating anions (e.g., AcO^- and OPNB^- (pK_a ca. 5 and 3.4, respectively)) did not promote the reaction at all, because they were not replaced by the allenamide, poorly coordinating analogues (i.e., SbF_6^- and OTf^-) caused the decomposition of the allenyl unit, probably via polymerization processes or hydrolysis.¹⁸ Finally, TsO^- anion with intermediate pK_a value (ca. –2.8) promoted the reaction to a very poor extent.

Note that no direct interaction among PPh_3AuTFA and **1a** was observed via ^1H , ^{19}F , and ^{31}P NMR investigation (CD_2Cl_2 , rt; see the Supporting Information), in the absence of allenamide¹⁹ which is taken into account by replacing the TFA^- from the coordination sphere of the metal. In addition, the inertness of **OMe-1a** under optimal conditions is in agreement with the postulated TFA^- /naphthol hydrogen-bond interaction during the reaction course of the process (Scheme 3c).

In conclusion, the gold(I)-TFA-catalyzed site-selective and stereoselective dearomatization of 2-naphthols with allenamides is documented. A range of C(1)-allylated naphthalenones is obtained in high yields under the synergistic action of the metal, as well as counterions.

■ ASSOCIATED CONTENT

§ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b03018.

Experimental procedures (PDF)

Analytic characterization of new compounds (PDF)

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Author Contributions

All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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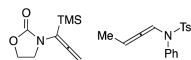
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