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New Chiral Binol-based Phosphates for Enantioselective [Au(I)]-catalyzed Dearomatization of β-Naphthols with Allenamides

Riccardo Pedrazzani,[a] Juzeng An,[a] Magda Monari[a] and Marco Bandini*[a,b]

Dedicated to our *dear friend* Franco Cozzi on the occasion to his 70th birthday

[a] Mr. R. Pedrazzani, Dr. J. An, Prof. M. Monari, Prof. M. Bandini
Dipartimento di Chimica "Giacomo Ciamician"
Alma Mater Studiorum – Università di Bologna
Via Selmi 2, 40126 Bologna
E-mail: marco.bandini@unibo.it
www.site.unibo.it/lasc
[b] Prof. M. Bandini
Consorzio C.I.N.M.P.I.S.
Via Selmi 2, 40126 Bologna

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Abstract: New chiral binol-based phosphate counterions have been synthetized, fully characterized and employed in the enantioselective gold catalyzed dearomatization of β-naphthols with allenamides. A range of densely functionalized C1-allylated naphthalenones were realized under mild conditions and high levels of chemo-, regio- and stereoselectivity (*ee* up to 95%).

The area of enantioselective dearomatization of arenes represents a challenging and highly performing research field within the synthetic organic chemistry scenario. Through this methodology, structurally elaborated 3D-polycyclic molecular scaffolds are directly accessible from their readily available flat 2D-congeners.[1] Despite the relatively young age, the field faced an exponential growth of attention over the past decade leading to several elegant and highly selective catalytic systems capable of performing the dearomatization of both carbon aromatics as well as heteroarenes through different synthetic "trajectories": metal catalysis, organo catalysis and photocatalysis.[2]

In this context, naphthols represent an inspiring platform to test new chiral promoters due to their key role in realizing natural and bioactive occurring structures.[3] In this segment, two main strategies can be highlighted namely: oxidative protocols (instauration of C-X bonds)[4] and dearomatization via C-C bond forming events (Figure 1a).[5] In both cases, a number of highly stereoselective protocols for the direct access to synthetically useful and densely functionalized naphthalenones have been documented (Figure 1b).[6]

In conjunction with our ongoing interests towards the implementation of catalytic dearomative protocols,[7,8] we recently documented on the use of achiral cationic [Au(I)] complexes for the intra-[9a] as well as intermolecular[9b] dearomatization of 2-naphthols by means of terminal/internal alkynes and allenamides. The latter approach highlights the crucial role of the counterion in homogenous gold catalysis, that is frequently underestimated in the reaction condition optimization.[10] In particular, trifluoroacetate (pK_a (TFA*H*) = 12.65, CH_3CN)[11a,b] displayed an adequate balance between metal coordination attitude and "hydrogen bond basicity" in order to co-assist the cationic gold promoted condensation via activation of the naphthyl core. Based on *p*Ka similarity between TFA^- (pK_a (TRIP*H*) = 13.60, CH_3CN) [11a,c] and chiral binol-based phosphates[7c] we envisioned the possibility to realize an enantioselective dearomatization variant of β-naphthols with allenamides[12] by adopting the chiral anion gold catalytic strategy (*Asymmetric Catalysis Direct Counterion* (ACDC)) applied to homogenous gold(I) catalysis.[13] As a matter of fact, the electrophilic activation of allenamides by cationic gold center would deliver an α,β-unsaturated iminium species **A** (Figure 1c) that, by establishing tight contact ion pairs with the chiral anion $\mathbf{L}^-$ could result into an optimal spatial arrangement to stereodifferentiate the two possible enantiotopic trajectories of the incoming naphthol.[14]

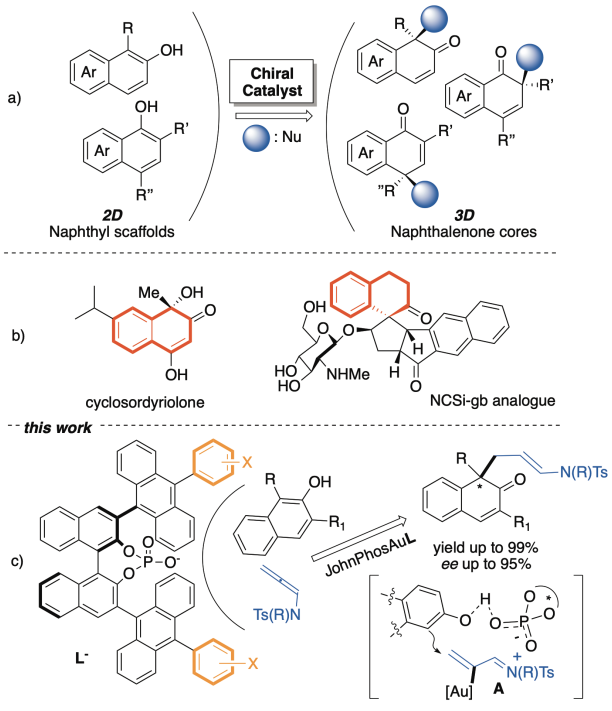
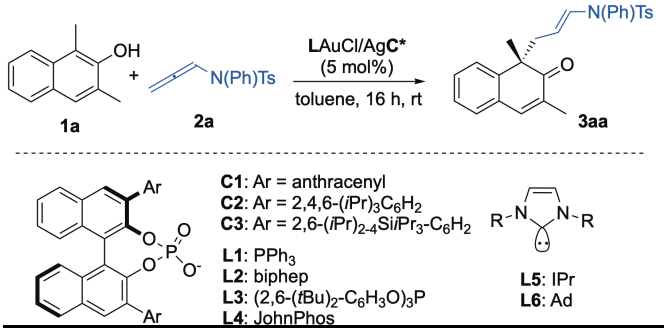


Figure 1. a) General strategies for the catalytic dearomatization of naphthols. b) Bioactive compounds featuring dearomatized naphthyl scaffolds; c) Working strategy of the present dearomative methodology.

In this work, our initial efforts towards the realization of new binol-based chiral gold counterions and their employment in the C1-site selective dearomatization of 2-naphthol (*ee* up to 95%) are summarized. It should be underlined that, during the realization of the work, a fully organic chiral Brønsted acid catalyzed enantioselective dearomatization of naphthols with allenamides was elegantly reported by Shao and coworkers.[15] This work, despite realising the desired products with excellent outcomes, resulted rather limited on the use of allenamides, being restricted to the substrate **2b** (*vide infra*). In this context we, planned to investigate a complementary approach based on the use of chiral counterions, that led us to design and synthetize structurally dedicated chiral binol-based phosphate scaffolds.

At the outset of our investigation 1,3-Me_2-β-naphthol **1a** and *N*-phenyl-tosyl allenamide **2a** were elected as model substrates for the desymmetrization reaction[16] and chiral binol-based counterions **C1-3**, deriving from commercially available phosphoric acids, were employed as discriminating agents in combination with PPh_3AuCl (5 mol%, toluene, rt, Table 1, entry 1-3). Delightly, naphthalenone (*S*)-**3aa** was obtained in a regio- and stereoselective manner (only γ-attack and *E*-configuration of the enamide unit were observed) and with enantiomeric excesses up to 75% in the presence of 3,3'-anthracenyl-phosphate **C1** (entry 1).

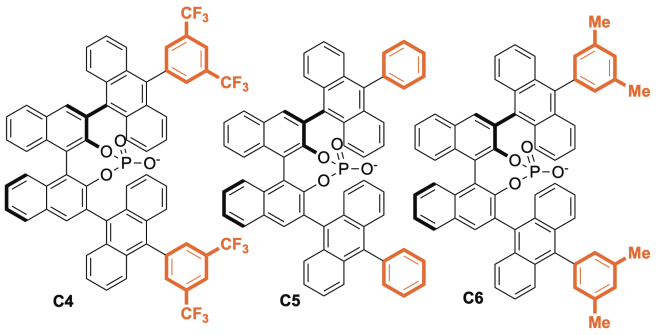
Table 1. Optimization reaction conditions.[a]



Run	L	C	Yield (%) **3aa**[b]	*Ee* (%) **3aa**[c]
1	**L1**	**C1**	79	75
2	**L1**	**C2**	53	72
3	**L1**	**C3**	70	62
4	**L2**	**C1**	56	80
5[d]	**L3**	**C1**	56	80
6	**L4**	**C1**	92	83
7	**L5**	**C1**	61	81
8	**L6**	**C1**	65	80

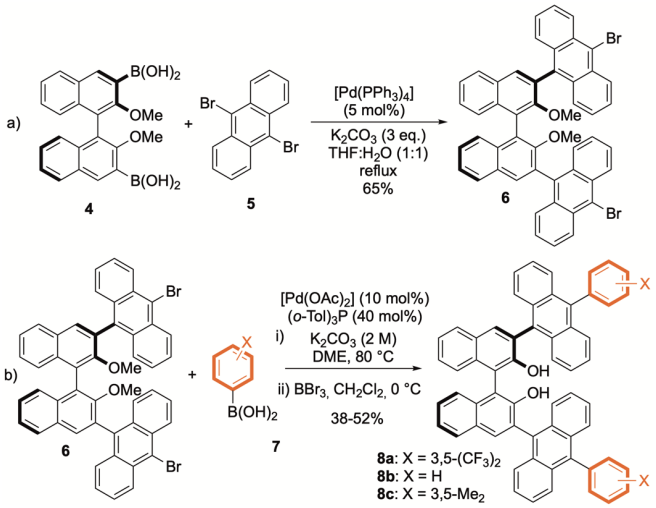
[a] All the reactions were carried out under nitrogen atmosphere, unless otherwise specified. [b] Isolated yields after flash chromatography. [c] Determined by chiral HPLC. [d] 2.5 mol% of the binuclear **L2**$(AuCl)_2$ was employed as the catalyst precursor. IPr: [1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene]; Ad: [1,3-bis(1-adamantyl)imidazol-2-ylidene].

Subsequently, the influence of the achiral gold ligand on the overall chemical and stereochemical outcome was assessed by running the model dearomatization with counterion **C1** and a range of gold ligands **L2-6** (entries 4-8). Although, comparable enantiomeric excesses were achieved (80-83%), almost quantitative isolated yield was recorded with JohnPhos **L4** (yield = 92%, entry 6). These findings prompted us to consider **L4** as the gold ligand for further investigations. Having counterion **C1** as a model chiral anion, we envisioned the possibility to reach higher stereoinductions by introducing longer and more sterically demanding aromatic sidearms at the 3,3'-positions of the binol scaffolds. In this direction, counterion **C4-6**, featuring 9,10-disubstituted anthracenyl pendants (Scheme 1), were designed with the aim of evaluating also the role of electronic properties of the chiral unit in controlling the stereoselectivity of the process.



Scheme 1. Second generation-type anthracenyl-based chiral gold counterions **C4-6**.

The unsubstituted enantiopure phosphate **C5** was initially targeted. The reported synthetic protocol by Birman and coworkers,[17a] involving a Suzuki-Miyaura cross-coupling to the 3,3'-functionalizations, faced serious issues of reproducibility in our hands, therefore a convergent synthetic pathway recently introduced by You and coworkers was utilized.[17b]

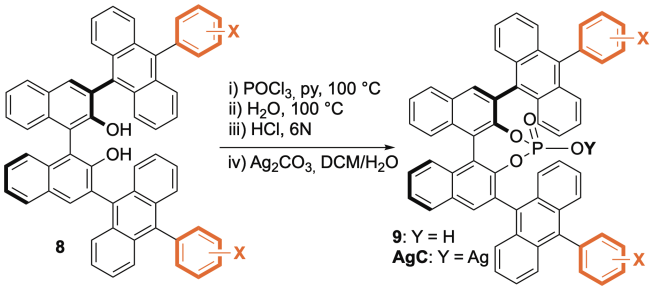


Scheme 2. Convergent synthetic approach for the realization of the 3,3'-substituted-binaphthyl derivatives **8a-c** (see supporting information for experimental details).

In details, the (*Ra*)-(2,2'-dimethoxy-[1,1'-binaphthalene]-3,3'-diyl)diboronic acid **4**[17c] was subjected to chemoselective [Pd(0)]

mediated coupling in the presence of 9,10-dibromoanthracene **5**, delivering the corresponding dibromo adduct **6** in 65% yield (Scheme 2a). Subsequently, compound **6** was condensed with the desired arylboronic acid **7** to deliver the 9,10-diarylanthracene scaffolds that were deprotected via classic BBr_3-promoted cleavage (overall yield 38-52%, Scheme 2b).

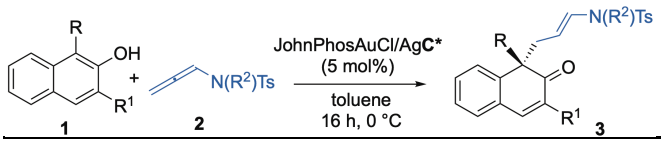
Therefore, the phosphorylative/hydrolysis sequence ($POCl_3$/py and HCl), led to the desired phosphoric acids **9** in acceptable overall yield. Finally, treatment of **9** with Ag_2CO_3 in a CH_2Cl_2/H_2O mixture provided the desired chiral silver salts Ag-**C4/6** in almost quantitative yield (91-94%, Scheme 3).



Scheme 3. Phosphorylation/hydrolysis/metal exchange synthetic sequence to the desired **AgC** salts (X: H, 3,5$(CF_3)_2$ and 3,5$(Me)_2$).

In order to properly assess the impact of the outer aryl group on the chemical as well as optical profile of the reaction, the model dearomative protocol was carried out in the presence of *in situ* formed JohnPhosAuCl/Ag**C4-6** (5 mol%) catalysts. The data reported on the Table 2 (entries 1-3) allowed the following conclusions to be drawn. Although similar enantiodiscrimination levels were observed (86-90%), a general trend towards increasing yields was recorded with 3,3'-sidearms carrying EDG substituents.

Table 2. Screening of second generation chiral counterions and generality of the protocol.[a]



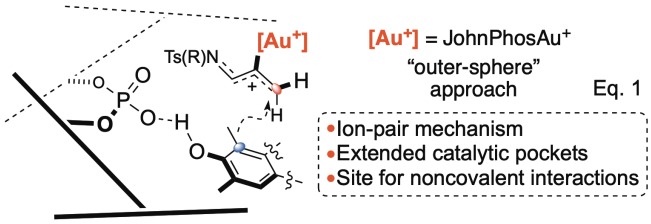
Run	R/R_1 (**1**)	R_2 (**2**)	**C***	Yield (%) **3**[b]	*Ee* (%) **3**[c]
1	Me/Me (**1a**)	Ph (**2a**)	**C4**	50 (**3aa**)	87
2	Me/Me (**1a**)	Ph (**2a**)	**C5**	75 (**3aa**)	86
3	Me/Me (**1a**)	Ph (**2a**)	**C6**	98 (**3aa**)	90
4	Me/Me (**1a**)	Ph (**2a**)	**9b**[d]	53 (**3aa**)	81
5	Me/H (**1b**)	Ph (**2a**)	**C6**	60 (**3ba**)	59
6	Bn/H (**1c**)	Ph (**2a**)	**C6**	47 (**3ca**)	55
7	Me/Et (**1d**)	Ph (**2a**)	**C6**	76 (**3da**)	83
8	Me/Br (**1e**)	Ph (**2a**)	**C6**	24 (**3ea**)	95
9	Me/Bn (**1f**)	Ph (**2a**)	**C6**	49 (**3fa**)	67
10	Me/Me (**1a**)	4-CF_3Ph (**2b**)	**C2**	40 (**3ab**)	43[e]
11	Me/Me (**1a**)	Me (**2c**)	**C6**	50 (**3ac**)	5

[a] All the reactions were carried out under nitrogen atmosphere, unless otherwise specifies. [b] Isolated yield after flash chromatography. [c] Determined by chiral HPLC. [d] In this reaction the gold catalysis was replaced by the chiral binol phosphoric acid **9b**. [e] The reaction was carried out in the presence of *in situ* formed JohnPhosAuCl (5 mol%) and (*R*)-Ag**C2** (5 mol%) as a halide scavenger.

In particular, quantitative yield was recorded when the CH_3-substitued counterion **C6** was utilized (entry 3). Although a conclusive rational for the latter outcome is still unavailable, we can speculate that the presence of electron-donating groups in the aryl sidearm could slightly but significantly increase the basicity of the phosphate anion with consequent enforcement of the key activating hydrogen-bond contact with the naphthol derivative (*i.e.* bifunctional catalysis, see Figure 1c). Therefore, to compare the catalytic performance of the present *enantioselective gold-catalysis direct counterion* methodology with a fully organic BA strategy,[14] the model reaction was carried out in the presence of the chiral phosphoric acid **9b** (5 mol%). Interestingly, although the previously reported efficiency of Binol-based phosphoric acid was confirmed (entry 4, Table 2), lower optical (*ee* = 81%) as well as chemical (yield = 53%) outcomes were recorded with respect to Au(I) catalysis.

Therefore, with the optimal conditions in hands, we faced the generality of the methodology by subjecting to the best conditions a range of differently substituted 2-naphthols (**1b-f**) and representative *N*-tosyl-allenamides **2b,c**. Concerning the naphthol substitution tolerance, the protocol showed a preference for 1,3-disubstitued arenes with respect to monosubstituted ones (entries 4,5). In the latter case, lower stereoinduction (up to 59%) was recorded. Interestingly, excellent enantioselection (*ee* = 95%) was obtained with 3-Br-naphthol (**1e**, entry 7), even if the presence of the halogen atom caused a significant drop in catalytic turnover (yield = 24%). The disappointing stereoselection observed with the *N*(Me)Ts allenamide **2c** clearly emphasized the key role of aromatic substitutions at the nitrogen atom in order to achieve satisfying stereochemical outcomes (entry 10). Finally, the absolute configuration of the major enantiomer was determined to be *S* by comparing the optical rotation value of the enantioenriched naphthalenone **3ab** (*ee* = 43%) with the one reported in literature.[14] Absolute configurations of the other dearomatized compounds **3** were assigned by analogy. This latter finding, in conjunction with the absolute (*E*)-configuration recorded in the C=C bond of **3**, suggested a tentative enantiodiscriminating approach between the allenamide and the naphthol as described in the Eq. 1. Here, the "*outer-sphere*"-type gold catalysis would result from the dual catalytic role played by JohnPhosAu**C***: involving the naphthol activation exerted by the chiral phosphate and consequent condensation on the *in situ* formed cationic allyl-gold species.[7f,18] The extended catalytic pocket[19] generated by the outer 3,3'-polyarene pendants is believed to account for the high stereoinduction observed due to the instauration of multiple sites for secondary noncovalent interactions.[20] Finally, to unambiguously prove the genuinity of [Au(I)] catalysis in the present methodology, we monitored the halide scavenger performance of the chiral silver salts by ^{31}P-NMR (d^8-toluene). Interestingly, by mixing JonphosAuCl (^{31}P-NMR = 59.18 ppm) and Ag**C4** (^{31}P-NMR = 11.41 ppm) the formation of a new species featuring shielded ^{31}P-signals (54.69

ppm and 6.90 ppm) was recorded and attributed to the catalytically active chiral JonhphosAu**C4** adduct.[21]



In conclusion, we have successfully developed an enantioselective allylating dearomatization of naphthols with allenamides by means of gold assisted *Asymmetric Catalysis Direct Counterion* strategy. A structure/reactivity correlation led us to design and realize some new densely functionalized 3,3'-polyacenes binol-based silver phosphates that provided the desired C1-substituted naphthalenones in *ee* up to 95%. Attempts to extend the presented enantioselective dearomative protocol to other aromatic compounds are currently under way in our laboratories and will be presented in due course.

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Keywords: Asymmetric catalysis • Gold catalysis • Dearomatization • Naphthol • Chiral counterion

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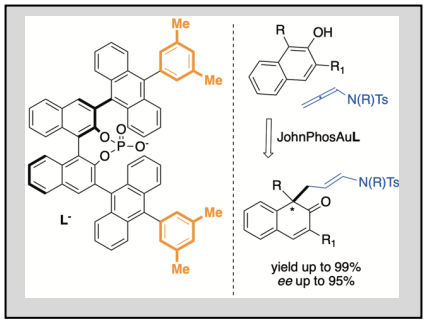

New chiral phosphate counterions are proposed in the enantioselective gold catalyzed dearomatization of 2-naphthols with allenamides. Densely functionalized naphthalenones (*ee* up to 95%) were obtained in the presence of chiral binol-scaffolds featuring EDG-containing 9,10-diarylanthracene (**L**, see Scheme).