DOI: 10.1002/adsc.200800628

# Ligand-Free Silver(I)-Catalyzed Intramolecular Friedel–Crafts Alkylation of Arenes with Allylic Alcohols

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Received: October 13, 2008; Revised: December 16, 2008; Published online: January 15, 2009

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.200800628.

**Abstract:** The silver-catalyzed direct activation of allylic alcohols as electrophilic partners for intramolecular Friedel–Crafts alkylation of arenes is described. Use of silver triflate (AgOTf; 10 mol%) enabled functionalized 1-vinyl-1,2,3,4-tetrahydronaphthalenes and a 4-vinyl-1,2,3,4-tetrahydroisoquinoline to be isolated in good yields with high levels of regiochemistry, under a ligand-free regime.

**Keywords:** alkylation; aromatic compounds; catalysis; Friedel–Crafts reaction; silver

Polycyclic aromatic compounds have risen to prominence in modern organic chemistry due to their presence in countless natural occurring compounds.[1] As a consequence, the demand for novel, mild and high yielding synthetic routes to their preparation is growing.[2]

Friedel–Crafts (FC) alkylation is probably the most reliable and powerful protocol for the elaboration of aromatic rings[3] and over the last few years, a great deal of attention has been devoted toward the design and development of new catalytic protocols with the aim of minimizing hazardous waste production.[4]

In this context, metal-catalyzed intramolecular allylic alkylations[5] deserve particular attention as they enable the creation of benzylic stereocenters in functionalized polycyclic aromatic compounds. Although several catalytic aromatic alkylations, employing allyl carbonates/acetates[6] and halides,[7] have been reported, the new frontier in the catalytic allylic alkylation of arenes concerns the use of allyllic alcohols as electrophilic partners. The great deal of interest for such unusual alkylation agents relies in their ready availability, atom economy and eco-sustainability (water is the only by-product of the reaction). However, together with these favourable features, the poor leaving group character and the strongly coordinating property of the hydroxy group have significantly limited the direct activation of alcohols in catalytic FC processes so far.

In this context, preliminary communications were confined to reactive electron-activated indoles,[8] and aromatic allylic alkylation was only very recently extended to simple arenes. In particular, gold(III) chloride proved to be efficient in the intermolecular alkylation of alkoxy-substituted arenes (large excess) in the presence of highly reactive secondary allylic alcohols.[9]

As a part of our continuing effort in developing new catalytic systems for aromatic functionalization,[6e,10] we decided to undertake a survey of transition metal salts with the aim of discovering suitable candidates for the intramolecular FC allylic alkylation of benzene-like arenes with direct activation of alcohols (Figure 1).[11]

Our working hypothesis concerned the use of metal complexes/salts featuring dual functions such as Lewis acidity and late-transition metal properties.[12] In this case, in fact, both the carbon-carbon double bond and the hydroxy group could be alternatively or simultaneously activated for the cyclization. Obviously, moderate oxophilicity is required in order to preclude the

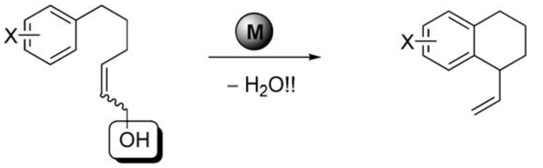
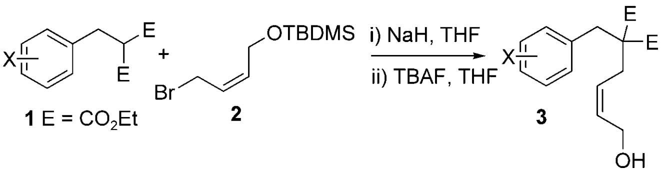


**Figure 1.** Working hypothesis for the metal-catalyzed intramolecular FC-type allylic alkylation of arenes.

deactivation of the catalyst *via* irreversible coordination to the hydroxy moiety.

It is worthy of note that, although intramolecular protocols are generally favoured with respect to the intermolecular analogous, catalytic intramolecular FC alkylations are cumbersome, due to the unfeasible use of the large excesses of one reaction partner, usually employed in bimolecular routes.

(*Z*)-Allylic alcohols **3** appeared good candidates to assess the scope of the process. In fact, a library of substrates carrying different aromatic decorations, can be readily synthesized starting from the corresponding aldehydes in four steps. Knoevenagel condensation and chemoselective reduction of the resulting C=C double bond[6e] led to **1** that were condensed with the (*Z*)-allyllic bromide **2**,[13] followed by removal of the TBDMS group (Scheme 1).

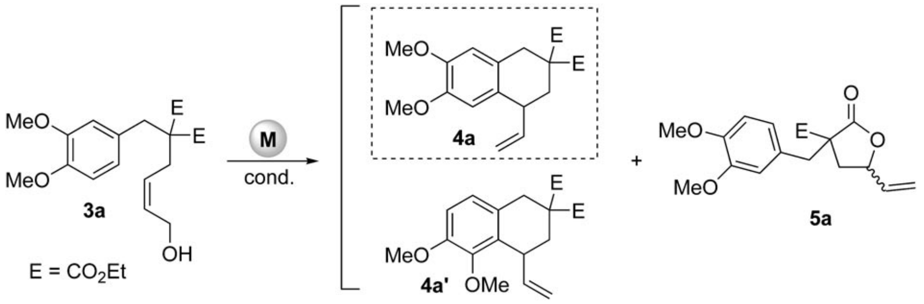


**Scheme 1.** Synthesis of the acyclic precursors **3**.

Inspired by the pioneering investigation of Kočovský and co-workers on the $[(acac)_2Mo(SbF_6)_2]$-catalyzed intermolecular alkylation of phenol and anisole,[14] we initially tested the readily available $[MoCl_4(CH_3CN)_2]$ (10 mol%) in the ring closing of (*Z*)-dimethoxyaryl alcohol **3a** (model substrate). Moderate conversions (56%, entry 1, Table 1) to **4a** were obtained in refluxing dioxane after 48 h. The addition of AgOTf to form cationic Mo species did not significantly improve the chemical outcome (conversion: 58%, entry 2). On the contrary, the addition of anhydrous HCl (5 mol%), as a Brønsted co-catalyst, led to **4a** in 73% yield (entry 3). However, in all the cases, the concomitant formation of lactone **5a** accompanied the desired FC alkylation product, in considerable amounts (17–30%).

Iridium(I) catalysis was also considered due to its capability of effecting intermolecular regio- and stereoselective alkylation of indoles with allyl acetates.[15] Interestingly, the combination of $[Ir(COD)Cl]_2$/P(furyl)$_3$ and AgOTf exhibits good catalytic activity, furnishing **4a** in 70% yield (**5a**: 10%). A higher conversion (80%) was obtained with the addition of 5 mol% of HCl and finally, the crucial role of the counteranion was verified by the reaction metathesis with $AgSbF_6$ (entry 6). However, the narrow generality in

**Table 1.** Optimization of the catalytic system for the intramolecular FC allylic alkylation of **3a**.[a]



| Entry | Catalyst [mol%] | Additive [%] | Conversion [%][b] **4a/4a'/5a** |
|---|---|---|---|
| 1 | $[MoCl_4(CH_3CN)_2]$ (10) | – | 56/0/30 |
| 2 | $[MoCl_4(CH_3CN)_2]$ (10) | AgOTf (20) | 58/0/27 |
| 3 | $[MoCl_4(CH_3CN)_2]$ (10) | AgOTf (20)/HCl (5) | 73/0/17 |
| 4 | $[Ir(COD)Cl]_2$/P(furyl)$_3$ (5/20) | AgOTf (10) | 70/0/10 |
| 5 | $[Ir(COD)Cl]_2$/P(furyl)$_3$ (5/20) | AgOTf (10)/HCl (5) | 80/0/5 |
| 6 | $[Ir(COD)Cl]_2$/P(furyl)$_3$ (5/20) | $AgSbF_6$ (10) | 10/0/50 |
| 7 | $RuCl_3$/dppb (10/10)[c] | AgOTf (30) | 0/63/28 |
| 8 | $PtCl_2$/dppb (10/10)[c] | AgOTf (20) | 60/10/10 |
| 9 | AuCl (10) | AgOTf (10) | 5/0/0[d] |
| 10 | $[(PPh_3)AuCl]$ (10) | AgOTf (10) | 83/0/0[e] |
| 11 | AgOTf (10) | – | 89/0/0[e] |

[a] All the reactions were carried out under nitrogen atmosphere for 48 h, under reflux with anhydrous solvents. Best solvents were as follows: Mo, Ir, Pt, Ru→dioxane, Au, Ag→dichloroethane.

[b] Determined by GC-MS.

[c] dppb = 1,4-bis(diphenylphosphino)butane.

[d] Large amount of alcohol **3a** was recovered unreacted.

[e] Isolated yield after flash chromatography. Reaction time 18 h.

scope was a major concern of Ir catalysis. Analogues aspects affected also the Pt and Ru catalysis, with the latter species ($RuCl_3$/AgOTf) furnishing the regioisomer **4a′** as the predominant product (entry 7).

Among the metal salts displaying dual functions Au(I)[16] and Ag(I) species have risen to prominence in catalytic organic transformations.[17]

Interestingly, in our model reaction, [($PPh_3$)AuCl]/AgOTf (10 mol%) led to **4a** exclusively in 83% yield (entry 10). More importantly, focusing on operational simplicity and costs of the process,[18] we were delighted to discover that the sole AgOTf (10 mol%), even in absence of stabilizing phosphine ligands, provided **4a** in 89% yield (DCE, reflux, 18 h, entry 11).

Worthy of mention is the divergent catalytic behaviour of gold and silver salts towards the presence of ligands. In particular, while ligand-free gold(I) catalysis led to unsatisfactory chemical outcomes (Table 1, entry 9), the addition of phosphines to AgOTf generated a general decrease in both reaction rate and chemoselectivity ($PPh_3$: yield = 12%; BINAP: yield = 72%, *ee* = 0%).

Contrary to the well recognized efficiency of Au(I) and Au(III) salts in catalytic functionalizations of arenes,[19] the potentialities of the slightly softer and low toxic silver salts, in Friedel–Crafts alkylation reactions, have not been explored to date.[20]

With optimal reaction conditions in hands, we further surveyed the scope of the process, by subjecting a range of acyclic aromatic precursors (**3b–m**) to ring closure, in the presence of AgOTf (10 mol%). Our results are summarized in Table 2.

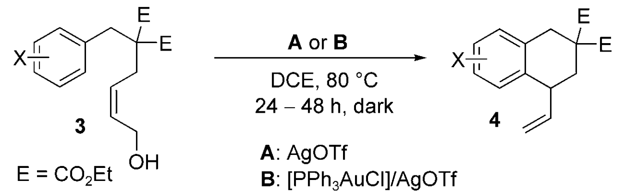
Firstly, the configuration of the carbon-carbon double bond of the acyclic precursor does not affect significantly the reaction outcome, with the (*E*)-**3a** alcohol leading to a comparably high isolated yield (90%, entry 1). Interestingly, both electron-rich (**3b–d**, **i**, **m**) and electron-neutral arenes (**3e–h**, **l**) reacted smoothly under the best conditions furnishing the corresponding functionalized 1-vinyl-1,2,3,4-tetrahydronaphthalenes **4** in moderate to good yields. High regioselectivity towards 1,4-ring-closure (14:1) was also obtained with substrate **3c** (entry 3).

For a better evaluation of the catalytic performances of AgOTf (method A), a series of comparative experiments was carried out with [($PPh_3$)AuCl]/AgOTf (10 mol%) (method B, Table 2).

In all cases higher isolated yields in **4** were obtained by ligand-free silver catalysis with the exception for alcohol **3j** in which the methylthio group probably deactivated the coordinatively unsaturated silver salt through irreversible coordination (entry 10).

Exemplary is the case of the ferrocenyl-containing alcohol **3k** that proved to be inert under gold-catalysis and provided the ring closing derivative **4k** in moderate yield (44%) and good diastereoselection with AgOTf (entry 11).[21]

**Table 2.** Silver triflate-catalyzed intramolecular FC allylic alkylation of aryl alcohols **3**.[a]



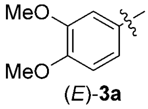
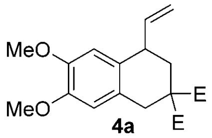
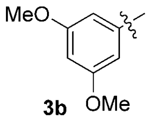
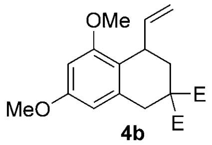
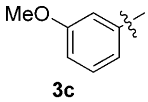
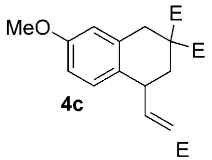
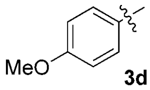
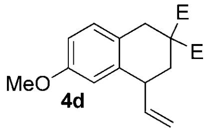
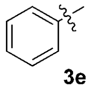
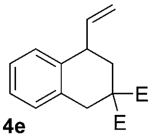
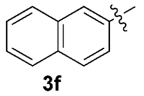
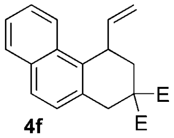
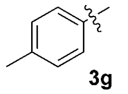
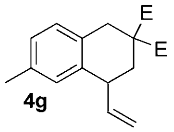
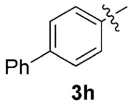
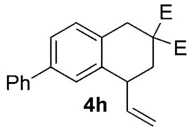
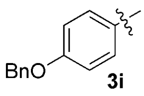
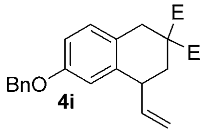
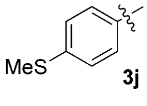
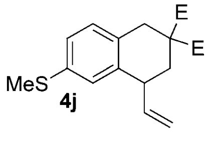
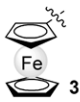
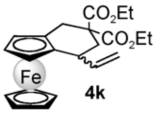
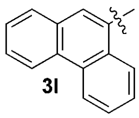
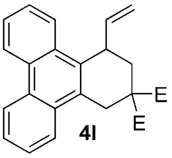
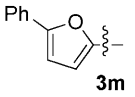
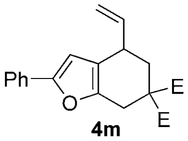
| Entry | Aryl group of **3** | Product **4** | Yield of **4** [%][b] | |
|---|---|---|---|---|
| | | | **A** | **B** |
| 1 |  (*E*)-**3a** |  **4a** | 90 | 85 |
| 2 |  **3b** |  **4b** | 70 | 55 |
| 3 |  **3c** |  **4c** | 67<br>(14:1)[c] | 58<br>(3:1)[c] |
| 4 |  **3d** |  **4d** | 77 | 60 |
| 5 |  **3e** |  **4e** | 73 | 47 |
| 6 |  **3f** |  **4f** | 80 | 52 |
| 7 |  **3g** |  **4g** | 76 | 60 |
| 8 |  **3h** |  **4h** | 56 | <5 |
| 9 |  **3i** |  **4i** | 55 | 50 |
| 10 |  **3j** |  **4j** | 53 | 63 |

**Table 2.** (Continued)

| Entry | Aryl group of **3** | Product **4** | Yield of **4** [%][b] A | Yield of **4** [%][b] B |
|---|---|---|---|---|
| 11 |  **3k** |  **4k** | 44<br>(80:20)[d] | –[e] |
| 12 |  **3l** |  **4l** | 73[f] | 28[f] |
| 13 |  **3m** |  **4m** | 65 | 28 |

[a] All the reactions were carried out under nitrogen atmosphere for 48 h, in DCE under reflux, unless otherwise specified. 10 mol% of catalyst was used.

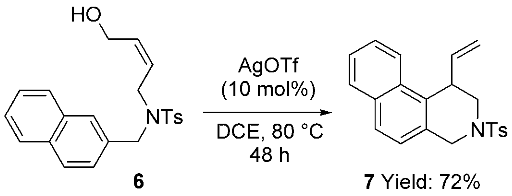
[b] Isolated yield after flash chromatography. In most cases the complete consumption of **3** occurred. Variable amount of the corresponding lactones **5** (10–25%) was formed.

[c] The regioisomeric ratio was determined by $^1$H NMR and GC-MS analyses.

[d] The diastereomeric ratio was determined by $^1$H NMR analysis. Reaction carried out with 20 mol% of catalyst. Reaction time 72 h.

[e] No reaction.

[f] Reaction time 16 h.



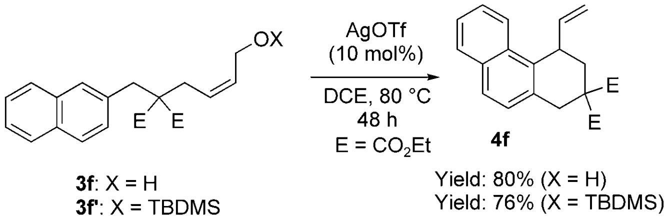
**Scheme 2.** Silver-catalyzed synthesis of tetrahydroisoquinoline **7** *via* intramolecular FC allylic alkylation.

The potentiality of the optimized catalytic system for the synthesis of pharmacologically active tetrahydroisoquinolines[22] was then surveyed. To this aim, the readily available allylic alcohol **6**[23] was treated with AgOTf (10 mol%) in DCE for 48 h. Interestingly, the desired cyclized compound **7** was isolated in 72% yield after flash chromatography (Scheme 2).

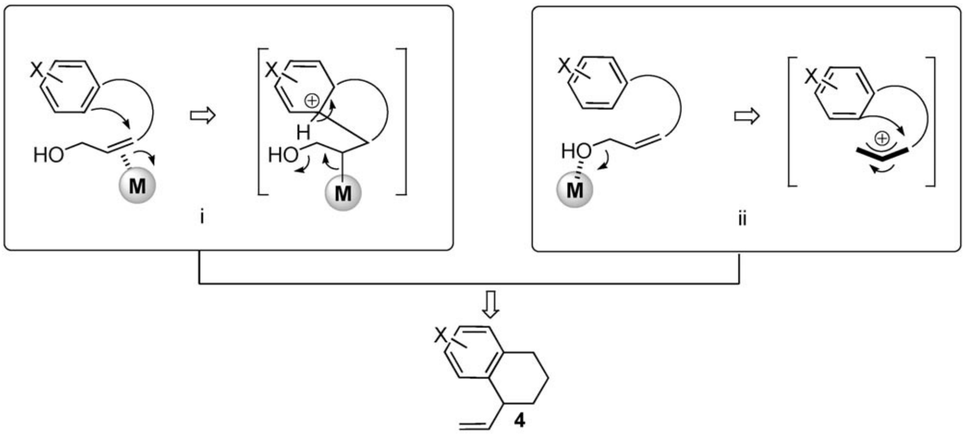
Cationic Ag(I) salts are known to readily interact with multiple C–C bonds.[20,24] Moreover, although to a less extent, the oxophilicity of silver salts has been exploited in organic reactions as well.[25] These aspects, combined with the possible formation of highly reactive allylic carbocationic intermediates, call for activation modes depicted in Scheme 3.

To gain insight into the plausible coordination mode of Ag(I)OTf, the optimal ring closing conditions were applied to *O*-TBDMS-**3f** (**3f′**) in which the possible coordination to the hydroxy group, should be denied by the presence of the sterically demanding *tert*-butyldimethylsilyl group (Scheme 4).

Here, although a conclusive mechanistic elucidation still remains elusive, the comparable isolated yields in **4f**, obtained with **3f** and corresponding silyl ether **3f′**



**Scheme 4.**



**Scheme 3.** Hypothetical coordination modes of silver to allyl alcohols **3**: i) Ag-olefin interaction; ii) allyl carbocationic intermediates.

(80% and 76%, respectively) calls for a coordination of the silver(I) to the C=C bond being active during the ring closing event (Scheme 3, path i).

In conclusion, a new, mild and environmentally friendly silver-catalyzed strategy for the intramolecular alkylation of aromatic rings, through direct activation of alcohols, is described. Further investigations addressing the inertness of electron-deficient arenes and the development of an enantioselective variant are currently underway in our laboratories.

## Experimental Section

### Typical Procedure for the Silver-Catalyzed Intramolecular Allylic Alkylation to Afford 4a

To a flamed-dried Schlenk tube equipped with a magnetic stirring bar, 1 mL of anhydrous $ClCH_2CH_2Cl$ (DCE) and 1.3 mg of AgOTf (5 μmol) were added. The tube was covered with an aluminium foil then a solution of (*Z*)-**3a** in DCE (50 μmol, 0.05 M) was added at once and the reaction mixture refluxed for 18 h in the dark. The volatiles were eliminated under reduced pressure and the crude residue directly purified through flash chromatography to afford a white wax; yield: 89%. $^1$H NMR (200 MHz, $CDCl_3$): δ = 1.21 (t, $J$ = 7.2 Hz, 3 H), 1.29 (t, $J$ = 7.2 Hz, 3 H), 1.98 (dd, $J_1$ = 11.8 Hz, $J_2$ = 13.8 Hz, 1 H), 2.59 (dd, $J_1$ = 4.0 Hz, $J_2$ = 11.8 Hz, 1 H), 3.10 (d, $J$ = 16.0 Hz, 1 H), 3.25 (d, $J$ = 16.0 Hz, 1 H), 3.45–3.56 (m, 1 H), 3.82 (s, 3 H), 3.87 (s, 3 H), 4.12–4.28 (m, 4 H), 5.16–5.26 (m, 2 H), 5.67–5.87 (m, 1 H), 6.63 (s, 1 H), 6.67 (s, 1 H); $^{13}$C NMR (50 MHz, $CDCl_3$): δ = 14.1 (2C), 34.7, 35.2, 41.4, 53.7, 55.9 (2C), 61.4, 61.7, 111.4 (2C), 116.3, 125.6, 128.1, 141.7, 147.6, 147.8, 170.8, 171.8; LC-MS: *m/z* = 363.0 (M+1), 747.2 (2M+Na); anal. calcd. for ($C_{20}H_{26}O_6$): C 66.28, H 7.23; found: C 66.25, H 7.20.

## Acknowledgements

*This work was supported by M.I.U.R. (Rome), Fondazione del Monte 1473, and University of Bologna. M.T. thanks NewChem S.p.A. for the financial support.*

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