π-Activated alcohols: an emerging class of alkylating agents for catalytic Friedel–Crafts reactions

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The direct functionalization of aromatic compounds, *via* Friedel–Crafts alkylation reactions with alcohols, is one of the cornerstones in organic chemistry. The present emerging area deals with the recent advances in the use of π-activated alcohols in the catalytic and stereoselective construction of benzylic stereocenters.

Introduction

The outstanding synthetic power of the Friedel–Crafts (FC) alkylation reactions, for the functionalization of arenes, is widely acknowledged.[1] However, over the last 130 years several aspects of the original version, mainly related to environmental concerns, had to be faced and overcome, to reach the actual worldwide application of FC processes both in industry and academy.

The type of alkylating agents (*i.e.* organo halides), together with the nature of the additives (*i.e.* large excesses of hazardous metal salts), render seminal FC processes impracticable in large scale production. The introduction of efficient and reusable solid Lewis/Brønsted acidic promoters or the possibility to use additives in substoichiometric amounts revolutionized the scenario, allowing for a marked drop in production/disposal of undesired waste during aromatic functionalizations.

Nevertheless, the replacement of organo-halides with widely available and more environmentally benign alcohols (water is the only by-product) in catalytic FC processes found it hard to emerge mainly due to the following aspects. (i) The poor leaving-group character of the hydroxy-moiety generally precludes the use of mild reaction conditions, such as low temperatures and mild additives. (ii) Deactivation of the FC-catalyst, *via* irreversible coordination to the hydroxy-group or *via* hydrolysis by water produced during the process, frequently occurs, leading to large excesses of additives being required.

It has been only recently that a partial solution to these aspects has been experienced by using π-activated alcohols in combination with unusual FC-catalysts, such as late-transition metal salts/complexes. Although sporadic findings have been appearing in the literature since the late 90s,[2] it is over the last five years (2004–2008) that an exponential growth in the number of examples has been recorded. Therefore, this *Emerging Area* addresses this period of time.

The term "π-activated" alcohols is commonly utilized to describe organic compounds carrying π-systems (*i.e.* carbon–carbon double/triple bonds, aromatic compounds or combinations) adjacent to the hydroxy group. This structural arrangement makes the C–OH bond activation easier, generally through the formation of stabilized positively charged intermediates. In this context, we found it convenient to gather the examples in three sections, categorizing the typology of the alcohols as: benzylic, propargylic

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and allylic alcohols (Fig. 1). Combinations of π-activating groups in the same molecule (X = Ar) are also frequently adopted to further increase the reactivity of the alkylating agent.

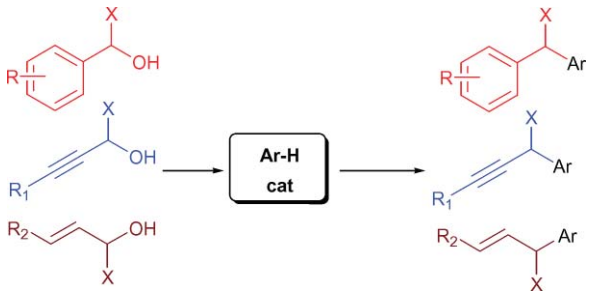


Fig. 1 Pictorial representation of π-activated alcohols in catalytic FC-alkylations. Combinations of benzylic frameworks with allylic and propargylic alcohols are possible when X = Ar.

An insight into the mechanistic details, if known, will also be highlighted. In this context, it is worth noting that most of these approaches involve carbocationic species as intermediates (S_N1-type mechanism) making the stereocontrol of the process a challenging task still largely unsolved.

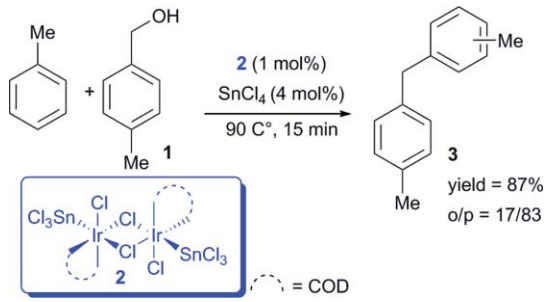
Benzylic alcohols

The benzylation of arenes is a classical and industrially useful Friedel–Crafts application to the synthesis of diarylmethanes. These molecular architectures are an integral part of several pharmacologically active compounds and are frequently utilized for the preparation of oligo- and polymeric organic electronics.[3] Here, the direct CH-functionalization of arenes represents a straightforward synthetic short-cut (no activating groups or additional protection/deprotection steps are required) in comparison to metal catalyzed cross-coupling reactions.

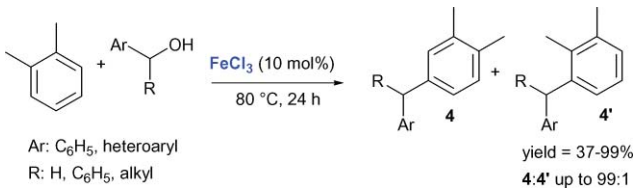
In this context, after the elegant work of Ishii and co-workers on the lanthanide triflate-catalyzed benzylation of electron-rich arenes with secondary alcohols (*i.e.* ArCH(OH)R),[4] a number of mild and high yielding catalytic routes to diarylmethanes have been described. Among them, it is worth noting the report by Roy and co-workers that emphasized the efficiency of hetero-bimetallic "Ir–Sn" catalysts in the process.[5] Here, the readily isolable complex $[Ir_2(COD)_2(SnCl_3)_2Cl_2(\mu\text{-}Cl)_2]$ **2** and the corresponding **2**–$SnCl_4$ aggregate proved to be better catalysts in terms of loading, arene/alcohol ratio, conversion, reaction time and selectivity in the reaction of benzene and toluene with a range of 1°, 2° and 3° alcohols. A representative example of the catalytic efficiency of the "Sn^{IV}–Ir^{III}" core is depicted in Scheme 1.

Almost simultaneously, Beller and colleagues documented the performance of $FeCl_3$[3] (10 mol%) in catalyzing the regioselective benzylation of *o*-xylene with a range of primary and secondary benzyl alcohols in excellent yields (up to 99%), without the need for exclusion of air and moisture (Scheme 2). Subsequently, the same team expanded this chemistry to other efficient catalytic systems such as $H_2[PtCl_6]\cdot H_2O$[6a] and $HAuCl_4$.[6b]

The recovery and reutilization of the promoting species is a fundamental aspect in modern chemical catalysis due to the growing demand for environmentally but also economically sustainable processes. To this end, the use of earth(III)perfluorinated salts



Scheme 1 Catalytic alkylation of toluene with benzyl alcohol **1** in the presence of hetero-bimetallic catalyst **2**–$SnCl_4$.



Scheme 2 Iron(III)-catalyzed regioselective benzylation of *o*-xylene with alcohols.

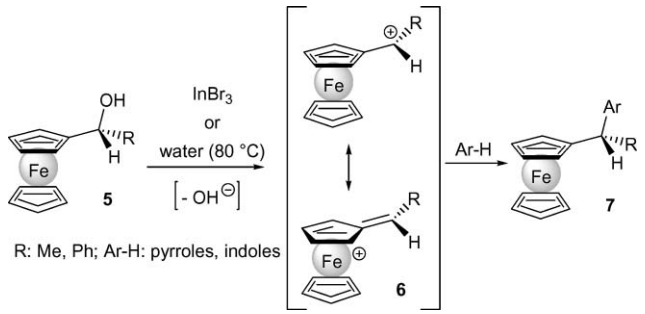
(*i.e.* $Yb(OSO_2C_8F_{17})_3$, 0.2 mol%) in fluorous biphasic systems (FBS) allowed the condensation of differently substituted arenes with 1° and 2° alcohols in moderate to good yields (41–96%).[7a] Again, the beneficial effect of imidazolium ionic liquids (*i.e.* [BMIM][OTf]), in the TfOH assisted (25–50 mol%) substitution of activated arenes with $PhCH_2OH$, was also documented.[7b] Interestingly, recycling and reuse of the active catalytic species was successfully proved, in consecutive runs, without significant loss in activity. Finally, Kobayashi and Shirakawa highlighted the role of surfactant-type Brønsted acid dodecylbenzenesulfonic acid (DBSA, 10 mol%) in the dehydrative benzylation and benzhydrylation of indoles with alcohols in pure water.[7c]

An analogous strategy was employed for the preparation of unsymmetrical diarylmethanes in the presence of $InCl_3\cdot 4H_2O$ (5 mol%) and acetylacetone (15 mol%).[8] The process exploits the strong dehydrating character of In(III) salts for the one-pot multibenzylation of arenes.

Stereoselective benzylation of arenes is still largely unexplored due to the loss of stereochemical information, during the reaction course, through the formation of planar carbocationic species (S_N1 *vs.* S_N2 mechanism).[4]

An interesting exception to this trend is represented by enantiomerically pure (1-hydroxyalkyl) ferrocenes **5** that, after dehydration, originate chiral cationic intermediates **6**. Such compounds have been successfully employed in the stereoretentive alkylation of indoles and pyrroles by Cozzi and co-workers, in the presence of $InBr_3$ (10–20 mol%)[9a] and "on water" (Scheme 3).[9b]

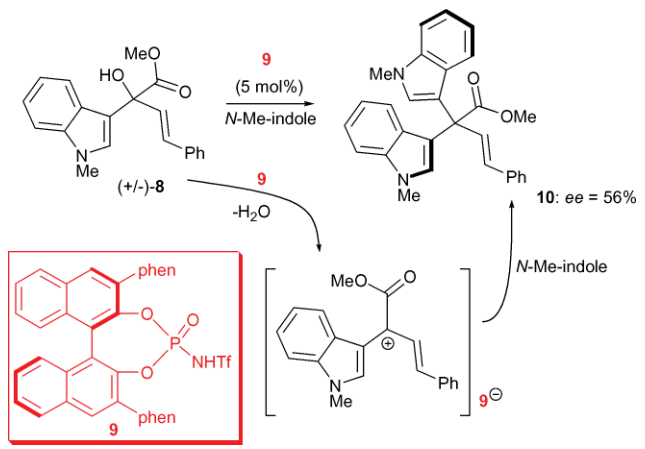
Interesting examples of diastereoselective FC-alkylations of electron-rich arenes (*i.e.* pyrroles, anisoles, furans, thiophenes and indoles), with chiral α-branched benzylic alcohols, were independently reported by Bach *et al.*[10a] and Chung *et al.*[10b] These approaches deal with the direct synthesis of enantiopure challenging poly-aromatic systems, however, stoichiometric amounts of Lewis or Brønsted acids were required. A very recent intermolecular stereoselective FC-benzylation of 1,3-benzodioxoles was elegantly applied, by Bach and Stadler, to the synthesis



Scheme 3 Use of enantiopure ferrocenyl alcohols **5** in the alkylation of heteroarenes.

of (–)-podophyllotoxin. In this process, a catalytic amount of $FeCl_3$ (5 mol%) was discovered to promote the FC-alkylation *via* chiral benzylic carbenium ions in a highly diastereoselective manner.[10c]

Finally, Rueping and colleagues, who in 2006 had communicated the inter- as well as the intramolecular bismuth(III)-catalyzed (1 mol%) benzylation of activated arenes with alcohols,[11a] reported the first enantioselective organo-catalyzed alkylation of indoles with benzyl alcohols.[11b] In particular, during the investigation of the stereoselective Michael-type addition of *N*-Me-indole to β,γ-unsaturated-α-keto esters, the unexpected formation of atropisomeric bisindole **10** was highlighted. The moderate but pioneering level of stereoinduction is interpreted in terms of tight contact ion pair formation between the conjugated base of the Brønsted acid **9** and the stabilized benzylic carbocationic intermediate (Scheme 4).



Scheme 4 Organo-catalyzed enantioselective synthesis of atropisomeric bisindole **10**.

Propargylic alcohols

The importance of persistent propargyl cations in FC-alkylations has long been known.[12] Propargyl cations, that are better represented with the corresponding allenylium species (Fig. 2), can be conveniently obtained from the corresponding alcohols by treatment with Lewis or Brønsted acidic sources. Due to the tendency of unsubstituted propargylic cations ($R_1 = R_2 = H$) to evolve towards polymeric compounds, 1-aryl-2-propyn-1-ol derivatives (**11**: $R_1 = Ar$) are generally employed in FC-substitutions.

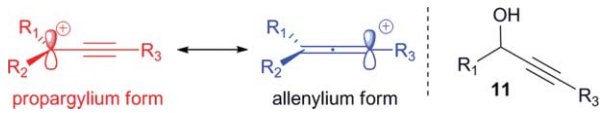
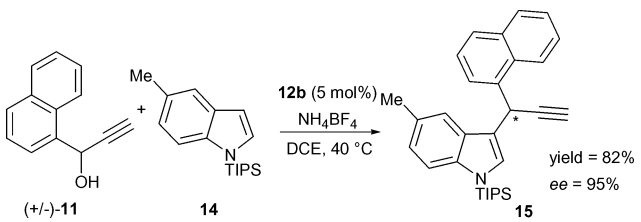


Fig. 2 Propargyl and allenyl resonance structures describing the propargyl cations ground state.

Nishibayashi and co-workers pioneered the metal-catalyzed propargylation of arenes and terminal alkynes with exceptionally active thiolate-bridged diruthenium complex **12a**.[13] Further investigations in this direction emphasized the attack of the aromatic ring to the γ-position of a cationic Ru-allenylidene intermediate **13**, exclusively (Fig. 3).[14] The generality in the scope of the process was demonstrated by realizing the regioselective FC-propargylation of several heteroaromatic compounds (*i.e.* furans, indoles, pyrroles, thiophenes) with 2-propyn-1-ols, both inter- as well as intramolecularly.

The first catalytic enantioselective FC-propargylation of 2-alkylfurans and *N,N*-dimethylaniline was carried out by Nishibayashi and co-workers, by replacing the former thiolate bridged-ruthenium-system **12a** with a new chiral complex (**12b**), carrying enantiomerically pure disulfide units (ee up to 94%).[15a] The scope of aromatic compounds was then extended to *N*-TIPS-indoles with excellent levels of enantiodiscrimination (ee up to 95%, Scheme 5).[15b]



Scheme 5 Representative example of Ru-catalyzed enantioselective propargylation of *N*-TIPS-indoles.

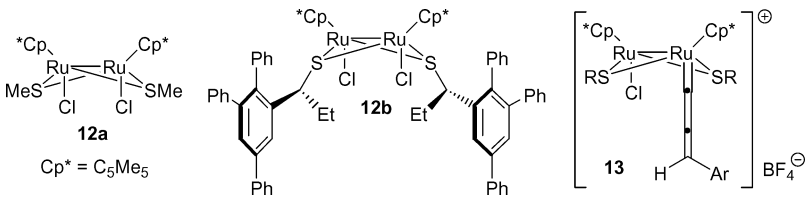
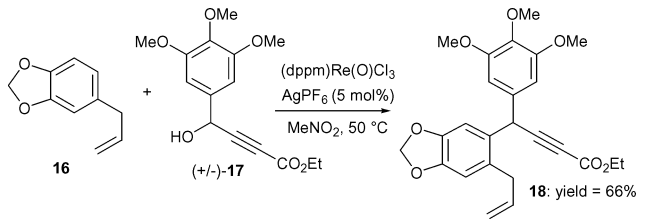


Fig. 3 Thiolate-diruthenium pre-catalysts (**12**) and intermediate **13** for the catalytic FC-propargylation.

The catalytic propargylation of aromatic compounds is a valuable and atom economical route to benzhydryl frameworks. For this reason, together with the former Ru-catalysis, numerous propargylic substitutions of arenes have been described.

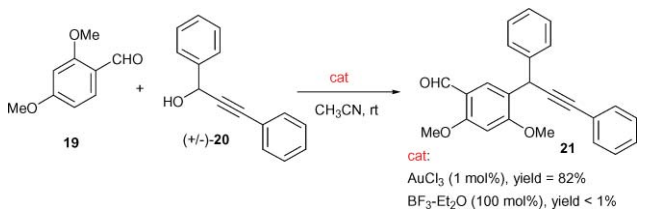
In this context, Toste and co-workers reported on the efficiency of (dppm)$ReOCl_3$ in promoting the alkylation of several electron-rich benzene-like compounds, with variously functionalized secondary internal propargyl alcohols.[16]

As a proof of concept, the successful Re-catalyzed propargylation of safrole **16** with propiolate **17** led to the benzhydryl compound **18** (yield = 66%), a valuable precursor of cytotoxic aryltertralin compounds (Scheme 6).



Scheme 6 Re-catalyzed propargylation of activated arenes.

The strong affinity of π-acidic Au(I) and Au(III) salts for triple C–C bonds, has emerged as an efficient tool for the catalytic addition of nucleophiles to alkynes. In this scenario, Campagne *et al.*[17a,b] and later Dyker *et al.*[17c] discussed the propargylic substitution of electron-rich arenes catalyzed by $NaAuCl_4 \cdot 2H_2O$ (5 mol%) and $AuCl_3$ (1 mol%), respectively. Exceptionally, the FC-alkylations worked smoothly at room temperature in the presence of secondary propargyl alcohols. While Campagne and co-workers reported only three examples of gold-catalyzed electrophilic aromatic substitutions (yields = 46–75%), Dyker and colleagues addressed in much detail the transformation, testing also challenging aromatic substrates such as pyrene and arenes carrying carbonylic moieties (**19**). Comparative experiments with BF_3·etherate (stoichiometric amount) underlined the real potential of $AuCl_3$ in FC-propargylation chemistry (Scheme 7).



Scheme 7 Gold(III)-catalyzed propargylation of arenes.

Efforts have also been devoted to the development of propargylic arene substitutions based on cheap and readily available catalysts. This goal would expand dramatically the feasibility of the present aromatic functionalizations to large scale production.

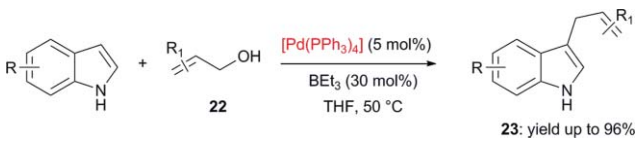
Zhan and co-workers reported the potentialities of $BiCl_3$ (10 mol%)[18a] and $FeCl_3$ (5 mol%)[18b] in the propargylation of arenes with alcohols, in the absence of air and moisture. Comparable catalytic performances were recorded for the two metal systems, with scope limitations to internal alcohols.

Despite impressive progress, there are still several limitations to the catalytic propargylic substitution of arenes. Among others, no examples of propargylation reactions with deactivated benzenes have been described so far, and propargylic alcohols carrying terminal alkyne groups or deriving from aliphatic aldehydes, still represent poor partners for FC-processes.[19] Although insights into the reaction mechanisms are still rare, in some cases a S_N2 mechanism is proposed even in the absence of concrete experimental evidence.[20]

Allylic alcohols

The regiochemical introduction of an allyl group into aromatic systems is a powerful synthetic tool due to its rapid and direct transformation in a plethora of key molecular motifs. Metal-catalyzed nucleophilic allylic substitution is probably the best strategy to obtain such a molecular architecture, however, catalytic allylation of arenes with alcohols has attracted considerable interest and undergone significant progress only recently. In this area, indoles are the most widely investigated aromatic system.

In contrast to propargylic substitutions, unsubstituted allyl alcohol (**22** R_1 = H) was proved to be a reliable FC-alkylating agent by Tamaru and co-workers. Their communication elegantly described the [Pd(0)]-catalyzed C-3-selective allylation of indoles in the presence of triethylborane (30 mol%, Scheme 8).[21] A broad scope of alcohols (α-, γ-methyl, and α-, γ-phenyl substituted **22**) and indoles was recorded and the catalytic system was efficiently utilized also for the synthesis of complex polycyclic indole-based alkaloids.



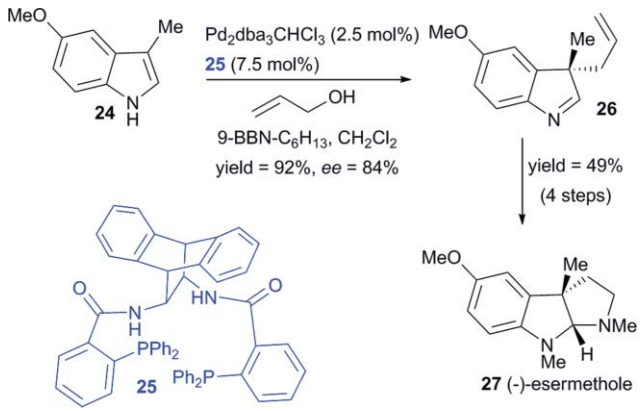
Scheme 8 Pd-catalyzed C-3 allylation of indoles promoted by BEt_3.

Mechanistically, it has been postulated that BEt_3 could coordinate the hydroxy-group of **22** favouring the oxidative addition to [Pd(0)].

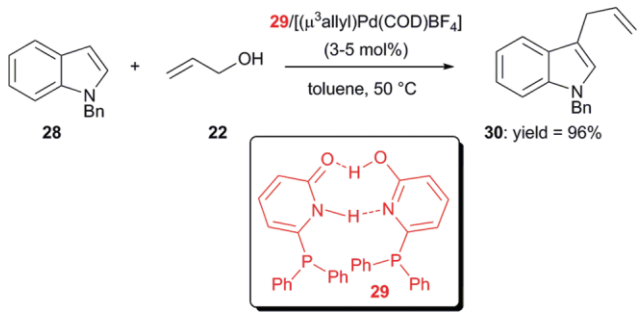
A strictly related enantioselective variant of this approach was later proposed by Trost and Quancard that targeted the alkylation of C-3 substituted indoles with allyl alcohol.[22] Interestingly, the use of a chiral Pd complex deriving from $Pd_2dba_3 \cdot CHCl_3$ and ligand **25** ([Pd] = 5 mol%), led to a range of functionalized indolenines carrying all carbon quaternary stereocenters, in good to excellent enantiomeric excesses (ee = 60–90%). The use of sterically crowded 9-BBN-C_6H_{13} as an additive supports the high C-3 *vs.* N-1 chemoselectivity observed. The synthetic utility of the method was then exemplified by incorporating the Pd-catalyzed enantioselective alkylation of **24** into the multi-step stereoselective synthesis of (–)-esermethole **27** (Scheme 9).

However the lack of final rearomatization when targeting exclusively 3-alkyl substituted indoles does not justify placing the method in the FC-process category.

The potentialities of Pd-catalysis renewed recently by Breit and co-workers with emphasis on the efficiency of self-assembled monodentate P-ligands in the allylation of *N*-heterocycles (indoles and 2-phenyl-pyrrole).[23] Interestingly, the complementary network of hydrogen-bondings, that drives the self-organizing events towards the desired bidentate ligands (**29**), is envisioned to assist the OH-cleavage of **22** during the reaction (Scheme 10).

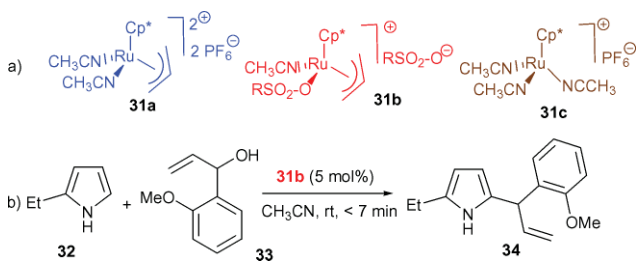


Scheme 9 Catalytic enantioselective allylation of C-3-substituted-1*H*-indoles.



Scheme 10 Representative example of direct Pd-catalyzed allylation of indoles with **22** by means of self-assembled bidentate ligands.

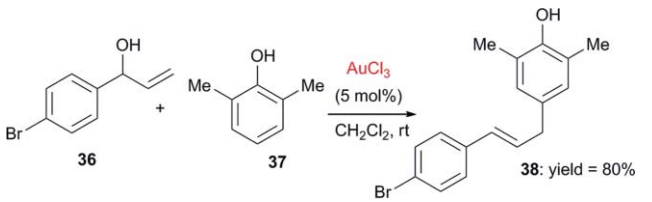
The know-how built up over the last decades in transition metal-catalyzed allylation reactions, has led to the efficient Ru-catalyzed functionalization of indoles with allylic alcohols. Pregosin and co-workers reported a series of interesting studies in which cationic Ru(IV)-complexes (**31**, Scheme 11a) enabled highly regioselective alkylation of indoles and pyrroles.[24] In particular, **31a** catalyzed efficiently the allylation of both electron-rich and electron-poor indoles with **22** in very short reaction times (<1 h *vs.* 20–64 h of Pd-catalysis) and at room temperature.[24a] The use of unsymmetrical secondary alcohols, such as ArCH(OH)CH=CH_2, introduces a need to control the branched–linear (*b–l*) ratio. Here, Ru-sulfonate (TSA or CSA) complex **31b** (formed *in situ* from the corresponding Trost catalyst **31c**) guaranteed the exclusive formation of the branched isomer (*b–l* ratio up to 71 : 1 with 2-ethyl pyrrole **32**) and short reaction times (7 min, Scheme 11b).[24b]



Scheme 11 (a) Cationic Ru(IV)-catalysts for FC-alkylations; (b) regioselective allylation of **32** through *in situ* formed Ru-sulfonate **31b**.

More favourable conditions for the allylation of electron-activated heteroarenes derived from the use of highly reactive 1,3-diphenyl-prop-2-en-1-ols (**35**) and analogues. In fact, the relative stability of the corresponding carbocationic species makes the C–OH bond cleavage more energetically feasible.

Numerous catalytic methodologies, utilizing **35**-type alcohols and indoles, have been described. Here, the efficiency of Lewis acids such as indium(III)X (X = Cl, Br),[25a,b] $FeCl_3$[25c] and $AuCl_3$[25d] was demonstrated. Catalyst loadings ranged from 1 to 10 mol% and in all cases good to excellent yields were accompanied by short reaction times. Among them, gold catalysis was successfully employed also in the allylic alkylation of electron-activated benzene-like arenes (*i.e.* phenols, anisoles, *m*-xylenes). When the FC-process was carried out with asymmetric allylic alcohols (*i.e.* **36**), the nucleophilic attack occurred exclusively at the less sterically encumbered center (Scheme 12).



Scheme 12 Au(III)-catalyzed and regioselective allylic alkylation of phenol **37**.

Friedel–Crafts alkylations in pure water are quite rare. Deactivation of the catalyst *via* irreversible coordination and decomposition of the reagents/intermediates account for this lack.

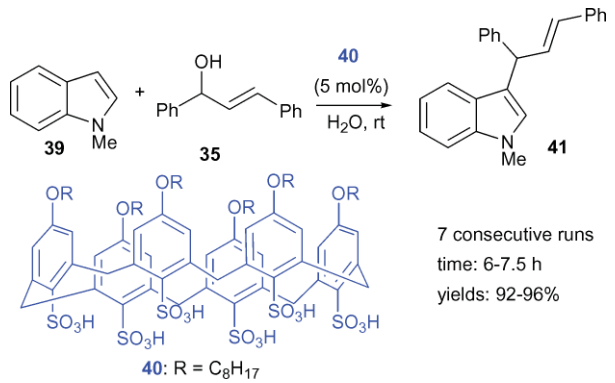
Liu and co-workers addressed such an issue, suggesting the use of calix[*n*]arene sulfonic acids as Brønsted-type promoters **40**.[26] The working hypothesis involves the creation of relatively small micelles in water, exploiting also the hydrophobic cavities of calixarenes. With this aim, several calix[*n*]arenes (*n* = 4, 6, 8), carrying sulfonate groups, were synthesized and employed as catalysts (1–5 mol%) in the FC-alkylation of aromatics and heteroaromatics with allylic alcohols in H_2O.

Important aspects for the final reaction outcome were the size of the cavity and the length of the alkyl chain R. Under the optimal conditions (R = C_8H_{17} and [*n*] = 6, calix-**40**), seven consecutive C-3 alkylations with **39**/**35** were successfully performed, with the same catalyst and without any apparent deterioration in activity (yields = 92–96%, Scheme 13).

Polycyclic aromatics are molecular architectures of primary importance in modern organic chemistry, due to their presence in countless natural occurring compounds. Cyclialkylation of aromatics is probably the most reliable and powerful protocol for a direct access to such systems. Interestingly, although acid promoted cyclizations of aryl-substituted alcohols have long been known, the field of catalytic aromatic cyclialkylations is still largely undeveloped.

At present only two reports address this topic.

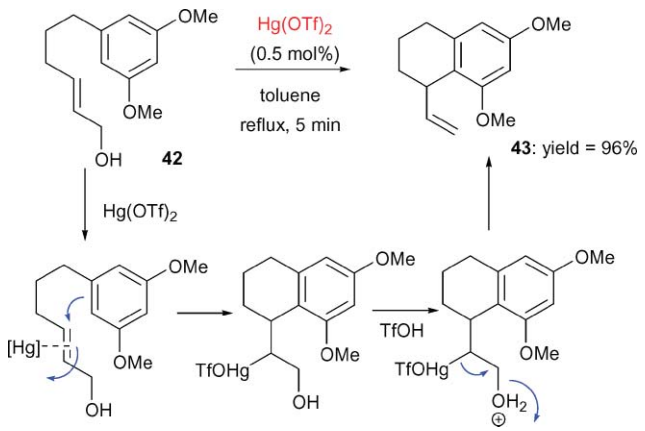
Firstly, Nishizawa and co-workers described the intramolecular allylic alkylation of acyclic aryl allyl alcohols **42** in the presence of $Hg(OTf)_2$ (0.5–1 mol%).[27] A range of bi- and tricyclic compounds were obtained in very high yields and short reaction times. Mechanistically, the authors hypothesized the initial π-coordination of the Hg(II)-salt to the carbon–carbon



Scheme 13 Brønsted-acid catalysis for the allylic alkylation of indoles in water.

double bond and subsequent hydroarylation with the electron-rich arene.

The organomercuric intermediate can then evolve into the final cyclized compound through a protonation–demercuriation step (Scheme 14).

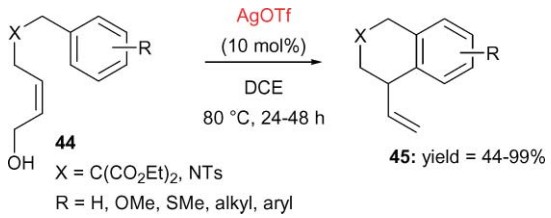


Scheme 14 Mercury-catalyzed FC cyclialkylation with alcohols.

Despite the excellent performance of the catalytic system, the use of mercury salts limits its synthetic potentialities.

In this context, very recently Bandini and Umani-Ronchi described an alternative catalytic approach for the preparation of tetrahydronaphthalenes and tetrahydroisoquinolines *via* ligand-free silver(I) catalysis.[28] The discovery of the catalytic activity of low toxic AgOTf, in promoting intramolecular FC-alkylation of neutral and electron-rich arenes, came from a survey of metal salts and reaction conditions. Generally, AgOTf promoted the reaction to a higher extent than other metal species. This finding was somehow surprising, as silver salts are mostly employed as halide abstractors in order to generate highly electrophilic metal-catalysts.

In particular, the treatment of alcohols **44** with 10 mol% of AgOTf ($ClCH_2CH_2Cl$, reflux, 24–48 h) led to the corresponding cyclic system in high isolated yield without the need for exclusion of air and moisture (Scheme 15). Also in this case, a C=C bond activation, *via* silver coordination, was postulated for the reaction.



Scheme 15 Ring-closing FC-alkylation of arenes catalyzed by AgOTf.

Conclusions

The reported examples emphasize the considerable attention that the use of π-activated alcohols in catalytic FC-processes has recently gained. Important issues such as mildness of reaction parameters, recovery/reusability of the catalytic system and chemo- and regioselectivity have been successfully and elegantly faced. However, major aspects such as stereocontrol and use of electron-deficient aromatic rings still require substantial efforts in order to provide practical and reliable solutions.

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