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Brønsted Acid-Catalyzed Carbocyclization of 2-Alkynyl Biaryls

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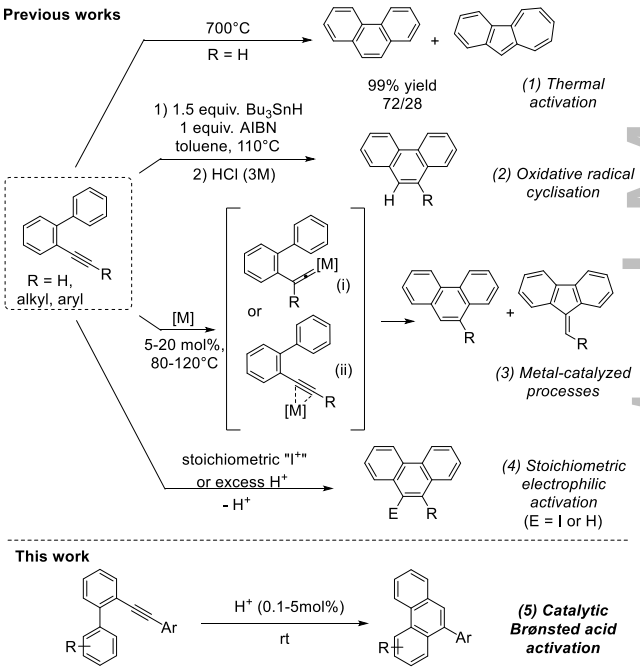
Abstract. Ortho-alkynyl biaryls react in the presence of catalytic amount of Brønsted acids to give phenanthrenes in high yields under mild conditions. The activity and selectivity of this transformation are governed by the substitution pattern of the diarylalkyne moiety. Selectivity shifts are observed between the carbophilic Lewis and Brønsted acid-catalyzed cycloisomerization involving alkyne activation.

Keywords: Alkynes; Brønsted acid catalysis; Phenanthrenes; Electrophilic activation; Cycloisomerization

The *6-endo* cycloisomerization of 2-alkynylbiphenyl represents one of the most straightforward methodology to access the phenanthrene core via an atom-economical route. Such intramolecular hydroarylation reactions have been thoroughly investigated via a large set of reactions conditions, reagents or catalysts.[1] The transformation of the parent substrate proceeds by thermal activation (700°C), to deliver quantitatively a mixture of phenanthrene and benzazulene (scheme 1, eq. 1).[2] This reaction has also been achieved via an oxidative radical cyclisation[3] in the presence of the Bu_3SnH/AIBN couple of reagents in toluene at reflux, followed by a protodestannylation in the presence of HCl (scheme 1, eq. 2). Metal-catalyzed cycloisomerizations of 2-alkynylbiaryls were extensively studied since the seminal work of the group of Fürstner.[4] Two competitive pathways involving either (*i*) a metal vinylidene intermediate[5] or (*ii*) carbophilic π-activation of the alkyne[6] have been proposed to explain the reactivity observed with the different transition metals (scheme 1, eq. 3). Regioselectivity of the cycloisomerization represents a major issue as dibenzofulvenes, resulting from a *5-exo* hydroarylation, were often observed as side products.



Scheme 1. Strategies for ortho-alkynylbiaryls cycloisomerisation reactions.

To date, significant catalytic activities have been obtained in the presence of metal salts or complexes obtained from the following elements: Pt,[4,7] Au,[4,8] In,[4] Ga,[4] W,[5b] Ru,[5a,9] Pd,[10] Nd,[11] Cu,[12] Ag,[13] Fe,[14] and Al.[15] In most studies, metal catalysts only operate at high

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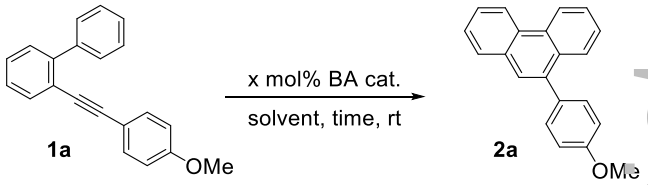
temperatures (from 80 to 120°C) with catalyst loadings ranging from 5 to 20 mol%. Stoichiometric amounts of electrophilic iodination reagents or excess Brønsted acids have also been reported as efficient mediators for this cycloisomerization of 2-alkynylbiaryls, following the early investigation of the group of Swager[16] on the use of main group electrophiles in these transformations[17] (scheme 1, eq. 4). Over the years, this methodology showed its versatility and allowed the synthesis of a variety of polycyclic aromatic hydrocarbon skeletons.[18] The phenanthrene moiety is also present in a large array of biologically active molecules[19] and in materials possessing electronic and optic properties.[16,20] Nevertheless, the use of a *catalytic amount* of Brønsted acid in this transformation was overlooked.[21] Considering the working hypothesis that some of the metal-catalyzed reactions may indeed proceed under hidden Brønsted acid catalysis,[22] we decided to engage in the study of the cycloisomerization of 2-alkynylbiaryls in the presence of Brønsted acid catalysts in order to assess the synthetic utility of this metal-free strategy.

As a model experiment, the cyclization of **1a** was engaged at room temperature in the presence of various Brønsted acids (Table 1). Using 5 mol% of trifluoromethanesulfonic acid[23] (TfOH) in dichloromethane, the obtention of phenanthrene **2a** in a quantitative yield was observed after 2h at room temperature. Full conversion was also observed with 5 mol% of bis(trifluoromethane-sulfonyl)amine (Tf_2NH) whereas 73% of conversion was obtained with 4-nitrobenzenesulfonic acid **3** after 70h of reaction (table 1, entries 2-3). Finally, no reaction was observed employing HCl as a catalyst (table 1, entry 4). Thus, TfOH was selected and the influence of the catalyst loading was further investigated. Full conversion and an isolated yield of 89% of **2a** was obtained using 0.1 mol% of this catalyst after 70 h, whereas 19% of ^{1}H NMR yield was observed using 0.01 mol% of TfOH after the same time, corresponding to a turnover number of 1900 (table 1, entries 5-6). Surprisingly, at low catalysts loadings, Tf_2NH, the strongest Brønsted acid, turned out to exhibit a lower activity (table 1, entry 7). Solvent effect was studied fixing the reaction time to 24 h: the reaction took place with full conversion in $CHCl_3$, toluene, cyclohexane and MeCN (table 1, entries 8-11). In contrast, total inhibition of the acid catalysis was observed in diethyl ether (table 1, entry 11). Using the procedure of Hintermann[22c] for the *in situ* formation of triflic acid from AgOTf and *tert*-BuCl in a 1:4 ratio, a good conversion was also observed (table 1, entry 13 *vs* 5).

Table 1. Optimization of reaction conditions[a]



Entry	Cat.	Cat. loading	Solvent	Time (h)	Conv.[b] (%)	Yield[c] (%)
1	TfOH	5	CH_2Cl_2	2	100	99
2	Tf_2NH	5	CH_2Cl_2	70	100	99
3	**3**[d]	5	CH_2Cl_2	70	73	n. i.
4	HCl	5	CH_2Cl_2	70	0	-
5[e]	TfOH	0.1	CH_2Cl_2	15	100	89
6[e]	TfOH	0.01	CH_2Cl_2	16	19	n. i.
7	Tf_2NH	0.1	CH_2Cl_2	15	27	n. i.
8	TfOH	5	$CHCl_3$	24	100	99
9	TfOH	5	toluene	24	100	99
10	TfOH	5	C_6H_{12}	24	100	80
11	TfOH	5	CH_3CN	24	100	99
12	TfOH	5	Et_2O	24	100	-
13	AgOTf/ *t*BuCl	1/4	CH_2Cl_2	4	80	n. i.

[a] Reaction run on 0.1 mmol of **1a** in 2 mL of solvent. [b] Determined by ^{1}H NMR analysis of the crude mixture. [c] Isolated yields after column chromatography on silica gel. [d] **3**: 4-nitrobenzenesulfonic acid. e) Reaction run using 5 mmol of **1a** in 20 mL of solvent. n. i.: not isolated.

Having these optimized conditions in hands, we decided to investigate the scope and limitations of this transformation (scheme 2). The reaction accommodated a variety of electron-donating groups on the distal aromatic ring (**2c-h**), but also worked with a phenyl substituent **2b**. The reaction proceeded with a modest 44% yield in the case of the 4-dimethylaminophenyl substituent under forcing conditions (**2i**), but failed with the free amino group (**1n**). The reaction also proceeded for substrate **1j** bearing a fluorine atom on the *para* position of the terminal phenyl ring. In contrast to the results obtained with aromatic rings bearing electron-donating substituents, no reactivity could be

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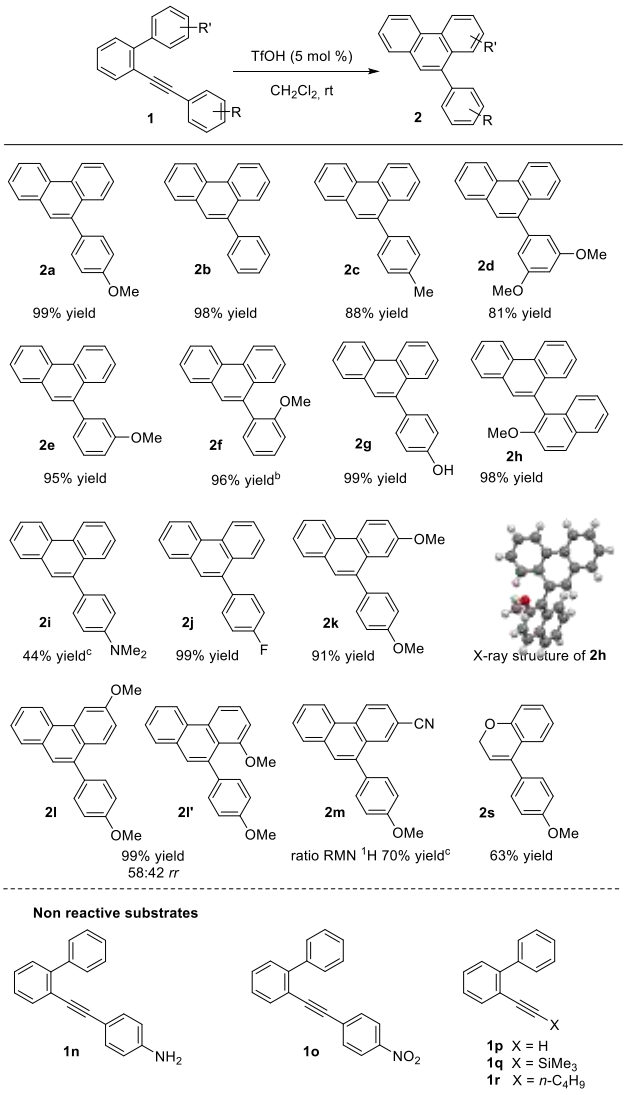
monitored with the para-nitro substrate (**1o**). Regarding the nucleophilic aromatic ring, electron-rich anisole derivatives gave excellent yields (**2k-l**) whereas electron-poor benzonitrile-containing substrate **2m** required harsher reaction conditions (80°C). Terminal alkynes and silyl-substituted substrates **1p** and **1q** exhibited no reactivity under these mild conditions.



[a] Reaction conditions: 0.1 mmol of substrate and 5 mol% of TfOH in CH_2Cl_2 (0.05 M). Isolated yield after column chromatography on silica gel. [b] 20 mol% of TfOH used. [c] Reaction run at 80°C in $(CH_2Cl)_2$ (0.05 M). *r.r.* regiomeric ratio.

Scheme 2. Scope of the Brønsted acid-catalyzed phenanthrene synthesis[a]

The catalytic conditions were also not compatible with the presence of an alkyl substituent on the terminal position of the substrate (see substrate **1r** for example). In contrast, a substrate possessing an internal alkyl substituent cleanly cyclized to deliver the corresponding 2*H*-chromene **2s** in good yield.

The chemoselectivity observed for these transformations was excellent and favors exclusively the aromatic carbon nucleophile over O-nucleophiles. For example, the formation of phenanthrene **2f** from substrate **1f** occurred selectively by a 6-*endo* cyclisation involving the aromatic ring (scheme 3, eq. 1). As the group of Alami[24] previously showed that tolane substrates bearing a 2-methoxy substituent could cleanly cyclize to give benzofuran products in good yields in the presence of a stoichiometric amount of *para*-toluenesulfonic acid (PTSA) in ethanol at 130°C under microwave irradiation, we treated substrate **1f** under these conditions and observed the formation of a mixture of the phenanthrene **2f** and benzofuran **5** resulting from the C- and O-nucleophile attack on the alkyne in a 77:23 ratio with a moderate conversion (scheme 3, eq. 2). More interestingly, when the free *ortho*-phenol substrate **1t** was reacted in presence of 5 mol% of TfOH, this alkyne was also cleanly transformed to the phenanthrene **2t** in 94% yield (scheme 3, eq. 3). This result under Brønsted acid catalysis was in sharp contrast when compared to the previously described metal-catalysed cyclisations.[25] Indeed, when treated with 20 mol% $PtCl_2$ at 80°C in toluene for 19 h, **1t** exclusively furnished the corresponding benzofuran **5** (99% yield, scheme 3, eq. 4). To continue the comparison with the carbophilic Lewis acid cyclisation of alkynylbiphenyls, we prepared the substrate **1u** used by Fürstner in his study of the transition metal-catalyzed synthesis of phenanthrenes.[4a] In the presence of 5 mol% $PtCl_2$ in toluene at 100°C for 24h, this derivative was reported to cyclize to deliver a mixture of the phenanthrene **2u** and the dibenzofulvene **6** in 87% yield and 60/40 regioisomeric ratio, resulting from a 6-*endo* and 5-*exo* cyclization respectively (scheme 3, eq. 5). Remarkably, in the presence of catalytic TfOH, the product was obtained in 91% yield as an unseparable mixture of **2u** and **6** in a 95/5 ratio.

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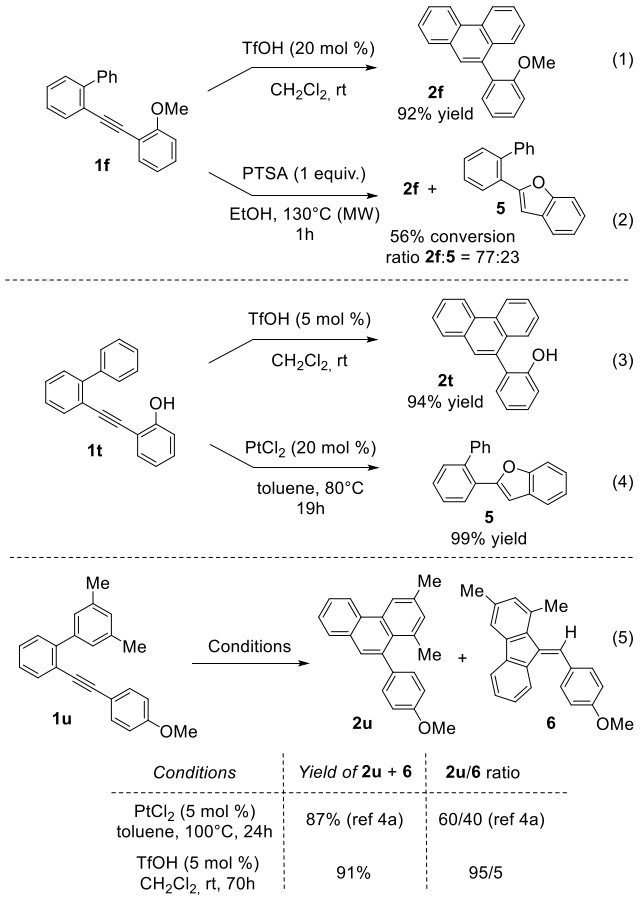


Scheme 3. Chemo- and regioselectivity of the Brønsted acid catalysed cyclization.

To further compare the activity of $PtCl_2$ and TfOH catalysts, the kinetics of the transformation from **1a** to **2a** (0.05 M) was recorded (Figure 1). With TfOH, the initial reaction rate was found to be of 1.23 10^{-3} mol.L^{-1}.min^{-1} at room temperature, whereas in the presence of $PtCl_2$ at 80° C, the reaction rate was only of 1.2 10^{-5} mol.L^{-1}.min^{-1}. Thus, with a difference of two orders of magnitude without taking in account the temperature effect, the TfOH catalytic system revealed to be much more active than the $PtCl_2$ one.

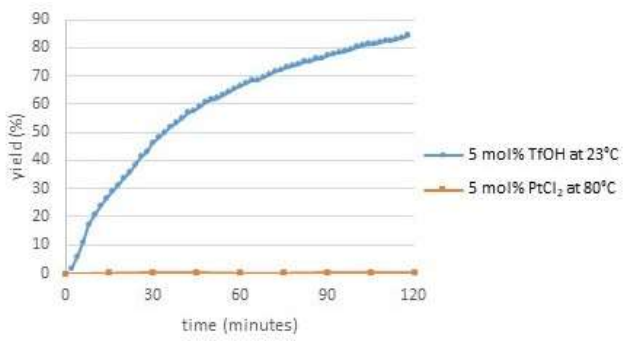
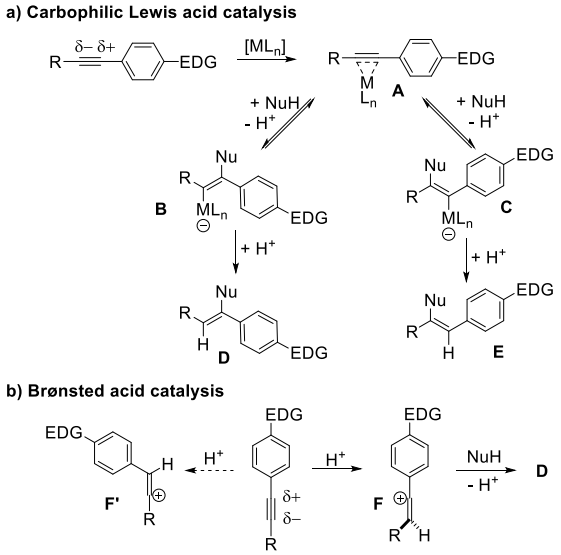


Figure 1. Reaction profile of the cyclization of **1a** to **2a** catalyzed by TfOH and $PtCl_2$.

Such observations go against the accepted view that carbophilic Lewis acids require softer reactions conditions and exhibit higher selectivities than Brønsted ones. In the case of 1,2-diarylalkynes substrates with carbophilic acids such as Pt, the formation of a π complex **A** between the metal fragment and the carbon unsaturation is observed (scheme 4). The polarisability of these Lewis acids induces a slippage of the metal fragment occurring reversibly on both ends of the C-C triple bond. The consecutive nucleophilic attack might therefore take places on both sites leading to a mixture of vinyl metal isomers **B** and **C**. Finally, protodemetallation completes the catalytic cycle and gives **D** and **E**.[6] This situation implies that depending on the stability of the final products, the use of these catalysts may lead to the selective formation of the *anti* Markovnikov product, as observed with **1r** and $PtCl_2$ (Scheme 3, eq. 4). On the other hand, the substitution pattern of the aryl groups, i.e. the presence of electron-donating groups, polarizes the C-C triple bond and thus induces its selective reaction with a proton delivering the vinyl carbocation **F**.[26,27] Trapping of this cationic intermediate with a nucleophile would deliver product **D**, i.e resulting from a 6-*endo* cyclization for 2-alkynylbiaryls substrates. For example, DFT calculations of vinyl cations **F** and **F'** revealed that intermediate **F** is more stable by 4.86 kcal/mol in the case of **1s** (see supporting information for details). These results explain that the 6-*endo* cyclization, corresponding to a Markovnikov addition, is strongly favored whereas the 5-*exo* cyclization hardly takes place in the Brønsted acid-catalyzed intramolecular arylation of diarylalkynes under these mild reaction conditions.



Scheme 4. Mechanistic rationale.

In conclusion, a mild and selective protocol for the synthesis of phenanthrenes from 2-biarylarylalkynes has been developed based on the use of catalytic amounts of Brønsted acids. This transformation occurs with high activity under very mild reaction conditions. The selectivity of the cyclization event is governed by the substitution pattern of the aromatic rings linked to the alkyne. These results point towards the necessity to revisit the involvement of Brønsted acid catalysis in metal-catalyzed cycloisomerization transformations involving alkyne activation and pave the way for the development of synthetic methodologies using Brønsted acid catalysis.

Experimental Section

General procedure for the Brønsted acid-catalyzed 2-alkynylbiaryls cycloisomerization

To a solution of 2-(arylethynyl)biphenyl **1** (0.1 mmol, 1 equiv.) in dichloromethane (1.5 mL) was added 0.5 mL of a solution of trifluoromethanesulfonic acid in CH_2Cl_2 (C = 10^{-2} mol.L^{-1}). The resulting mixture was stirred at room temperature. After completion of the reaction as checked by TLC, the mixture was quenched with an aqueous saturated solution of $NaHCO_3$ (2 mL) and extracted three times with DCM. The combined organic phases were dried over anhydrous Na_2SO_4 and concentrated under vacuum to give product **2**.

CCDC-1828671 contains the supplementary crystallographic data for compound **2h**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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