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Facile synthesis of indene and fluorene derivatives through $AlCl_3$-catalyzed cyclization of in situ formed iminium ions

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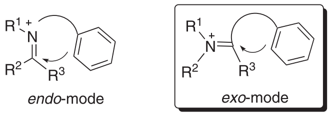
A simple $AlCl_3$-catalyzed condensation/cyclization cascade process between aldehydes and sulfonamide is reported, in which two new bonds and one five-membered ring are simultaneously formed with water as the byproduct. This method provides a rapid access to indenamine and 9-aminofluorene derivatives. Additionally, these products can be transformed into corresponding indanones and fluorenones under the developed conditions.

KEYWORDS
$AlCl_3$, exo-model cyclization, fluorene, iminium ion, indene

1 | INTRODUCTION

The development of simple and efficient methods for the synthesis of carbo- and heterocyclic molecular scaffolds continues to be a principal issue in synthetic chemistry. In this context, the iminium ion cyclization reaction has proven to be an extremely useful approach for the rapid and convergent construction of complex structures.[1] One such example is the Pictet-Spengler reaction, an invaluable method being widely used in both laboratory and industry for the preparation of a diverse array of isoquinoline and indole alkaloids.[1,2] Despite the cyclization reactions involving iminium ions have led to profound developments in synthetic chemistry, where, very often, they focused on the construction of nitrogen-containing heterocycles through an *endo*-model.[2,3] In sharp contrast, the *exo*-model cyclizations leading to the formation of all-carbon ring skeletons have received considerably less attention (Scheme 1), the reports pertaining to this class of reaction remain scarce.[4]

Indene and fluorene are two important classes of structural motifs present in a number of naturally occurring molecules and pharmaceutically useful compounds.[5] Moreover they also serve as valuable building blocks in material science and ligands in organometallic chemistry.[6] For example, the fluorenyl-based Pd complexes and the indenyl-based Ni complexes have been used as efficient catalysts in Suzuki coupling and olefin polymerization reactions, respectively.[6] Consequently, these unique carbocycles have and continue to receive significant synthetic interest. To date, a number of effective strategies for the synthesis of various indene or fluorene derivatives have been developed.[7,8] Despite these advances, catalytic protocol to construct both of indene and fluorene skeletons is absent in the literature. In addition, many existing methods more or less have suffered from some drawbacks, including the necessity of expensive transition metal catalysts, special starting materials and lengthy synthetic sequences. Therefore, development of simple and atom-economic methodologies to furnish these structural motifs is still in high demand.



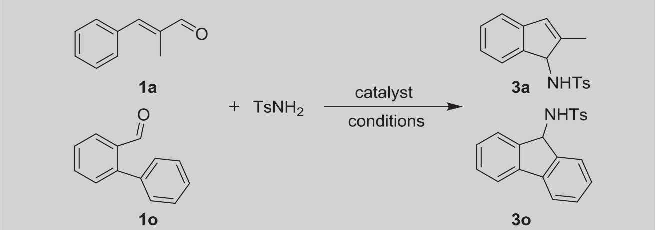
SCHEME 1 Cyclization models of iminium ion

Aluminum chloride ($AlCl_3$) has attracted the attention of synthetic organic chemists for a long time, since it is a cheap, easy available and less toxic Lewis acid and has been found to show promising catalytic abilities in a number of organic transformations, such as Friedel-Crafts reaction, Diels-Alder reaction, Michael addition, Prins reaction, [3 + 2] cycloaddition, ring expansion, and cascade arylation/cyclization, etc.[9] In recent years, our group has been interested in the development of eco-friendly methods for the synthesis of C-C, C-N bonds and carbocycles through functionalization of the C-O/C=O bonds.[10] As part of our ongoing program on this area, herein, we report an $AlCl_3$-catalyzed two-component cascade reaction between aldehydes and sulfonamide that provides a facile access to indenamine and 9-aminofluorene derivatives. Additionally, derivation of these compounds was also investigated, we found that indenamine and 9-aminofluorene can be transformed into corresponding indanone and fluorenone under the developed conditions.

2 | RESULTS AND DISCUSSION

Recently, our group disclosed a novel $FeCl_3$-catalyzed cascade process to construction of indene frameworks via condensation of the readily accessible cinnamylaldehydes and sulfonamides.[4d] In continuation of this research, we began to wonder about the possibility of using this protocol to synthesize both indene and fluorene skeletons. Initially, we subjected 2-phenylbenzaldehyde (**1o**) to the optimized reaction conditions identified in our previous work (Table 1, entry 1).[4d] However, reaction of **1o** with $TsNH_2$ gave an intractable mixture rather than the corresponding cyclization product of 9-aminofluorene (**3o**) even at room temperature, presumably due to the instability of **3o** under the catalysis of $FeCl_3$.[11] Recently, the iron-catalyzed cleavage of the C-N bond of benzylic sulfonamides has emerged as a useful strategy in C-C bond formation reactions.[12] Inspired by the previous works,[9] $AlCl_3$ was then selected as the catalyst. To our delight, both **1a** ((*E*)-2-methyl-3-phenylacryl-aldehyde) and **1o** can react smoothly with $TsNH_2$ in nitromethane to give the desired cyclization products (Table 1, entry 2). Encouraged by this result, the reaction conditions were then systematically investigated. These examinations revealed that treating **1a** or **1o** (1.0 equiv.) with 1.2 equiv. of $TsNH_2$ in CH_3NO_2 in the presence of 20 mol% $AlCl_3$ gave the best results (Table 1, entries 4 and 5). Under the optimized reaction conditions, the desired cyclization products **3a** and **3o** could be isolated in 90% and 81% yields, respectively. Replacing $AlCl_3$ with $FeCl_3$, the reaction of **1o** with $TsNH_2$ in CH_3NO_2 also resulted in an inseparable mixture (Table 1, entry 12). Other Lewis acids, such as $TiCl_4$, CuI, $BiCl_3$, $ZnCl_2$, $BF_3{\cdot}OEt_2$ and $Cu(OTf)_2$, were found to be less effective or ineffective in promoting this transformation (Table 1, entries 13–18). Further investigation of this reaction under an argon atmosphere had no obvious influences on the yields (Table 1, entry 19). In addition, hydrochloric acid showed no catalytic activity in this transformation, which suggests that the present reactions is catalyzed by $AlCl_3$ rather than its hydrolyzed species (Table 1, entry 20).

TABLE 1 Optimization of reaction conditions[a]



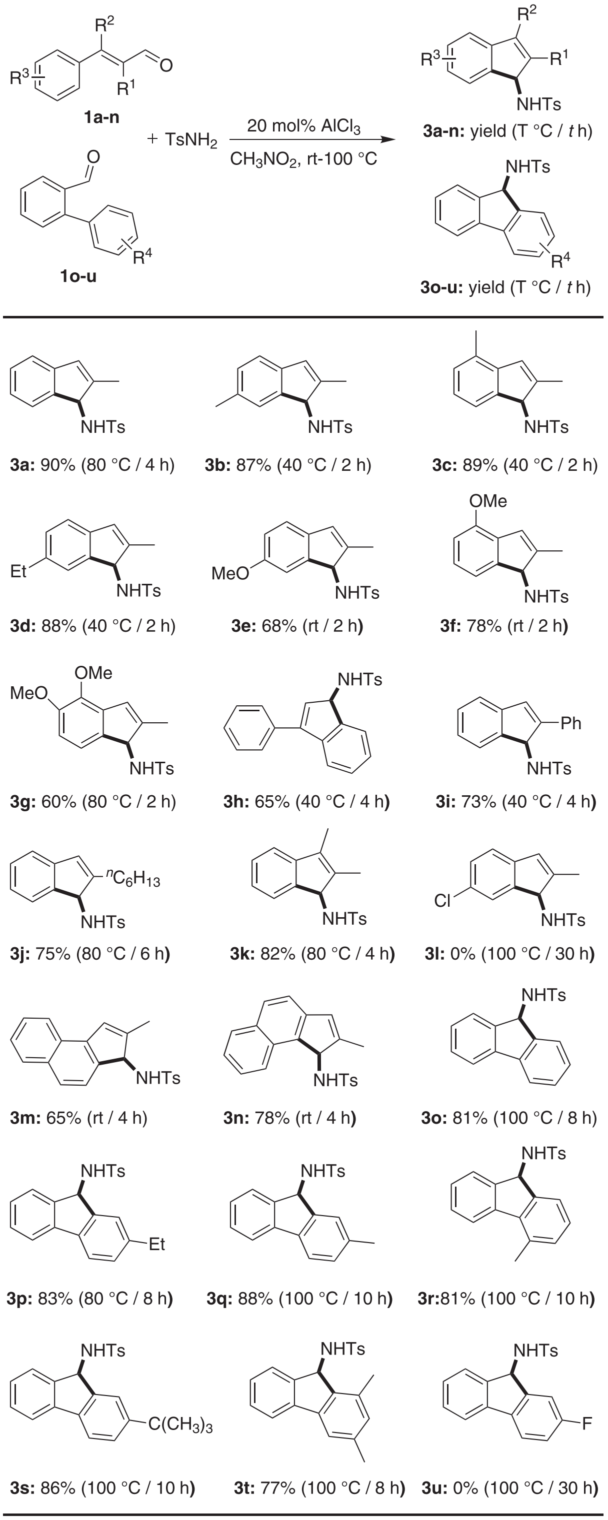
Entry	Catalyst (mol%)	Solvent	T (°C)	Yield (%)[b] / *t* (h)	
				3a	3o
1	$FeCl_3$ (20)	Toluene	40	98/4h	Mess/0.5h
2	$AlCl_3$ (10)	CH_3NO_2	80	45/4h	30/16h
3	$AlCl_3$ (15)	CH_3NO_2	80	60/4h	51/16h
4	$AlCl_3$ (20)	CH_3NO_2	80	90/4h	80/14h
5	$AlCl_3$ (20)	CH_3NO_2	100	89/4h	81/8h
6	$AlCl_3$ (30)	CH_3NO_2	80	85/4h	77/14h
7	$AlCl_3$ (20)	Toluene	80	75/4h	Trace/12h
8	$AlCl_3$ (20)	EtOH	80	0/8h	0/12h
9	$AlCl_3$ (20)	DCM	40	42/8h	16/12h
10	$AlCl_3$ (20)	THF	60	0/12h	0/12h
11	$AlCl_3$ (20)	DCE	80	37/8h	10/24h
12	$FeCl_3$ (20)	CH_3NO_2	100	64/4h	Mess/2h
13	$TiCl_4$ (20)	CH_3NO_2	80	Mess/8h	Trace/12h
14	CuI (20)	CH_3NO_2	80	0/4h	0/12h
15	$BiCl_3$ (20)	CH_3NO_2	80	30/8h	Trace/12h
16	$ZnCl_2$ (20)	CH_3NO_2	80	0/8h	0/12h
17	$BF_3{\cdot}Et_2O$ (20)	CH_3NO_2	80	58/4h	Mess/2h
18	$Cu(OTf)_2$ (20)	CH_3NO_2	80	38/4h	26/16h
19[c]	$AlCl_3$ (20)	CH_3NO_2	80	88/4h	82/14h
20	HCl (20)	CH_3NO_2	80	0/4h	0/12h

[a] Reaction conditions: **1a** (0.3 mmol), $TsNH_2$ (0.36 mmol), solvent (3 mL).

[b] Isolated yield.

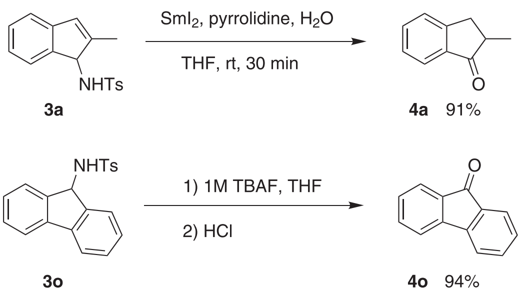
[c] Under argon.

With the optimized reaction conditions in hand (Table 1, entry 3), the generality of this $AlCl_3$-catalyzed reaction was then investigated on a series of aldehydes. As shown in Scheme 2, the optimized reaction conditions show good substrate compatibility with a wide variety of cinnamylaldehydes and arylated benzaldehydes, providing the corresponding indene and fluorene derivatives in moderate to good yields (**3a–k**; **3m–t**). However, the starting cinnamylaldehyde has an α-substituent is crucial to this reaction, for example, *(Z)*-cinnamaldehyde and (*E*)-3-phenylbut-2-enal can not take place this transformation even under harsh reaction conditions. The only exception to this structural requisite is the aldehyde (**1h**) that can carry out this reaction successfully without an α-substituent, presumably due to its stereoconvergent structure. These results are consistent with our previous observations.[4d] In addition, the electronic natures of the substrates also have obvious influences on the reaction outcomes. When aldehydes **1l** and **1u** bearing an electron-withdrawing group on the phenyl ring were subjected to this transformation, the cyclization reactions were totally inhibited, only corresponding imines along with the unreacted aldehydes were observed; in contrast, when electron-donating substituents such as alkyl or methoxy groups were placed on the phenyl ring, the reaction could carry out at 40 °C or room temperature within a short reaction time (**3b–f**). However, the methoxy group substituted substrates gave relatively low yields (**3b** and **3e**; **3c** and **3f**), whereas increasing the catalyst loading led to inferior yields. The reason for this phenomenon is unclear, we think that the electronic properties and the coordination abilities of these substrates should be responsible for the observed results.[13] In addition, 1-naphthyl and 2-naphthyl substituted acroleins **1m** and **1n** can also be applied to this reaction, providing a facile method to access benzene-fused indene type of tricycles (**3m–n**), which are also useful carbocyclic skeletons.[14] To our disappointment, aromatic and cinnamic ketones such as (*E*)-3-methyl-4-phenylbut-3-en-2-one and 2-acetylbipheny can not undergo this transformation even under harsh reaction conditions, which can probably be attributed to the lower electrophilicity of the ketone.



SCHEME 2 Reaction of $TsNH_2$ with various aldehydes

Subsequently, derivation of the cyclization products was carried out using **3a** and **3o** as the substrates. However, removal of the tosyl-moiety from **3a** and **3o** proved much more challenging, continued efforts to achieve this goal under a variety of conditions[15] (SmI_2, sodium naphthalide, Mg/CH_3OH, LAH/THF, $NaOH/CH_3OH$) failed to give the deprotected products. Surprisingly, upon treatment of these compounds with SmI_2/pyrrolidine/water[16] in THF, **3a** was smoothly transformed into indanone **4a** in 91% yield without the formation of detosylation product (Scheme 3), whereas

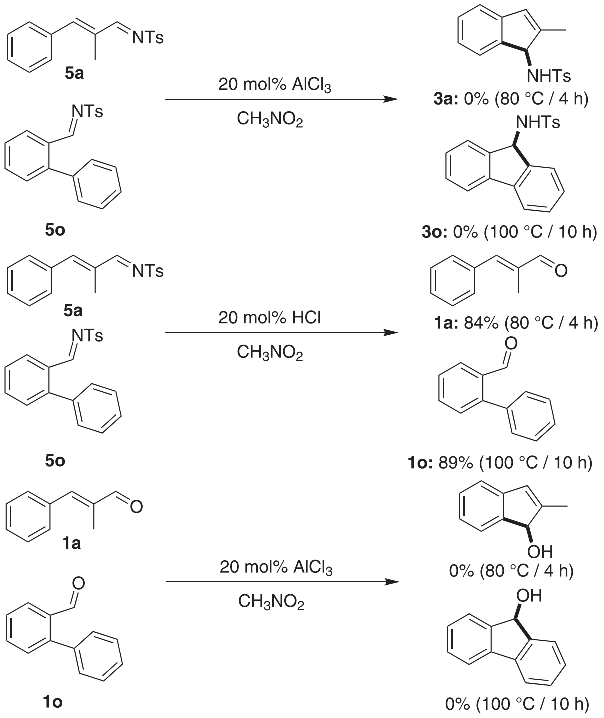


SCHEME 3 Formation of indanone **4a** and fluorenone **4o**

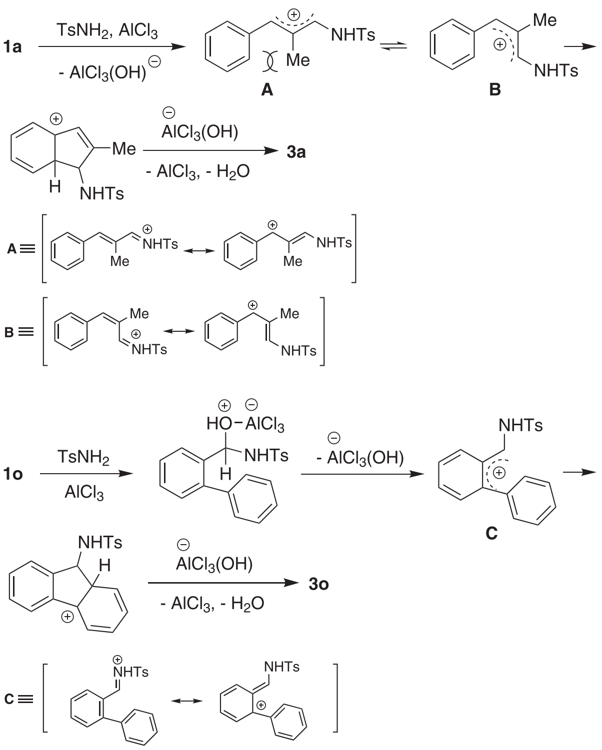
3o led to an inseparable mixture. Other indenamine derivatives such as **3k** can also efficiently undergo this transformation. The mechanism for this transformation is not clear at this stage,[17] further experimental and mechanistic studies are underway in our group. In the case of **3o** which can be readily converted into corresponding fluorenone **4o** upon treatment with tetrabutylammonium fluoride (TBAF).[18]

With the aim of understanding the mechanism, control experiments were conducted (Scheme 4). First, prior-prepared aldimines **5a** and **5o** were subjected to this reaction under the optimal conditions. Strikingly, both **5a** and **5o** failed to give the cyclization products **3a** and **3o** even under improved reaction temperature and prolonged reaction time, which led to partially decomposition of **5a** and **5o** into corresponding aldehydes. Second, treating **5a** and **5o** with 20 mol% of hydrochloric acid, most of them were hydrolyzed into **1a** and **1o** without the formation of **3a** and **3o**. Third, leaving aldehyde **1a** or **1o** in typical reaction conditions without addition of $TsNH_2$, no reaction was observed.

Based on the above results and previous works,[13,4] a tentative reaction pathway is described in Scheme 5. Initially, $AlCl_3$-catalyzed condensation of the aldehyde **1a** (or **1o**) and $TsNH_2$ leads to the formation of resonance-stabilized iminium ion **A** (or **C**), **A** can isomerize to its *Z* isomer **B**. Subsequently, intermediate **B** (or **C**) undergoing an intramolecular aza-Friedel-Crafts reaction or a 4π electrocyclization process would give rise to the corresponding cyclization product. In the case of aldehyde **1a**, isomerization of intermediate **A** through bond rotation to give its *Z* isomer **B** is necessary before cyclization can occur. We speculate that this process is facilitated by the cinnamylaldehyde bearing an α-substituent, which has an $A_{1,2}$ strain between the α-alkyl and the aromatic group. Additionally, formation of the delocalized cationic species would also benefit from the α-alkyl due to its electron-donating nature.



SCHEME 4 Control experiments



SCHEME 5 Proposed mechanism

3 | CONCLUSIONS

In summary, an $AlCl_3$-catalyzed two-component cyclization reaction between aldehydes (i.e. cinnamylaldehydes and arylated benzaldehydes) and sulfonamide for the convenient synthesis of fluorene and indene derivatives has been developed. The advantages of this method include readily available starting materials, cheap catalyst, simple reaction conditions, and atom-economic way. Additionally, this method can also be used as an alternative for the synthesis of indanones and fluorenones. Further refining this method in organic synthesis is in progress in our laboratory and will be reported in due course.

3.1 | Experimental

To a stirred solution of aldehydes **1a-1u** (0.3 mmol) in CH_3NO_2 (3 mL) was added 4-methylbenzenesulfonamide (0.36 mmol, 61.6 mg) and $AlCl_3$ (20 mol%, 8.0 mg). The resulting mixture was stirred at rt-100 °C. After the aldehyde was completely consumed (monitored by TLC), the reaction was quenched by addition of H_2O (3 mL) and then extracted with ethyl acetate (3 × 5 ml). The combined organic layer was washed with brine, dried over Mg_2SO_4 and filtered. The solvent was removed in vacuo, and the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc =10/1) to afford the corresponding products. See the supporting information for details.

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