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Assembly of homoallylamine derivatives through iron-catalyzed three-component sulfonamidoallylation reaction

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An efficient $FeCl_3$-catalyzed three-component reaction between aldehydes, sulfonamides and allylsilanes has been achieved, which provides a convenient, atom-economic and green way to construct homoallylamine derivatives. In addition, this reaction exhibits excellent *syn* stereoselectivity with γ-substituted allylsilanes.

Additional supporting information may be found in the online version of this article at the publisher's web site.

Keywords: multicomponent reaction; iron; homoallylamine derivatives; sulfonamidoallylation; imine

Introduction

Imine and iminium ions are reactive building blocks with diverse applications in organic chemistry for the construction of α-functionalized amino derivatives and nitrogen-containing heterocycles.[1] Representative examples of these transformations are three-component Mannich reactions and Pictet–Spengler tetrahydroisoquinoline synthesis, which have become powerful synthetic tools in both the laboratory and industry.[1,2] Although a significant number of α-amidoalkylation reactions with the imine or iminium ion serving as an electrophile have been developed in the past 100 years, the catalytic versions of three-component amidoallylation reactions using silicon-based nucleophiles for the synthesis of homoallylic amines are rather limited.[3–6] In general, these compounds are prepared by addition of a metallic allyl reagent such as allyl Sn, Sm, In, Zn and B to a prior-prepared imine species.[7] Obviously, catalytic three-component amidoallylation reactions involving *in situ* formed imines and non-toxic allylsilanes are much more step- and atom-economical as well as environmentally benign. However, despite several efficient catalytic systems for such transformations have been developed in the past decade, most of them need a relative expensive Lewis acid such as metal triflate and oxo-rhenium(VII) as the catalyst.[3,4a–c]

Considering that homoallylamines are fundamentally important building blocks for the synthesis of many natural products, pharmaceuticals and useful nitrogen-containing compounds,[8] further exploration of cheap and environmentally friendly catalysts for this transformation would be valuable. Very recently, we reported a two-component procedure for the construction of indene frameworks, via an iron-catalyzed *in situ* formed *N*-sulfonyliminium ion-initiated intramolecular alkylation.[9] In continuation of our study of the examination of iron as a promising catalyst in C–C and C–N bond formation,[10,11] we extended the reaction mentioned above to a three-component version (Scheme 1). To the best of our knowledge, this iron-catalyzed three-component cascade reaction has not been reported previously. In this paper, we report the results of our study of this reaction.

Results and discussion

Initial experiments were carried out on the reaction of benzaldehyde (**1a**; 1.0 equiv.) with *p*-toluenesulfonamide (**2a**; 1.5 equiv.) and allyltrimethylsilane (**3a**; 1.3 equiv.) in dichloromethane at room temperature with $FeCl_3$ (5 mol%) as catalyst. To our delight, the reaction proceeds smoothly to give the sulfonamidoallylation product **4a** in 53% yield, which can be markedly improved by increasing the reaction temperature and catalyst loading (Table 1, entries 1–4). Further investigation of the solvent effect indicates that the nature of the reaction media significantly affects the reaction (Table 1, entries 5–12), with dichloromethane being the most suitable solvent. With respect to substrate loading, a 1:1.5:1.3 ratio of **1a** to **2a** to **3a** gives the best result. Under these optimized reaction conditions, the desired product **4a** can be isolated in 94% yield (Table 1, entry 3). On replacing $FeCl_3$ with $FeCl_3{\cdot}6H_2O$, the reaction gives a lower yield (77%; Table 1, entry 13). Other iron salts and Lewis acids prove to be less effective or ineffective in promoting this transformation (Table 1, entries 14–20). Control experiment indicates that a catalyst is essential for this reaction (Table 1, entry 21). In addition, several Brønsted acids (e.g. TfOH and HCl) were also examined for this reaction. Unfortunately, only a trace amount of **4a** is observed when using triflic acid as the catalyst; other Brønsted acids are completely ineffective for this transformation (Table 1, entry 22).

With the optimized reaction conditions in hand (Table 1, entry 3), the substrate scope and limitations of this reaction were then investigated using a series of aldehydes (Table 2). It is found that the

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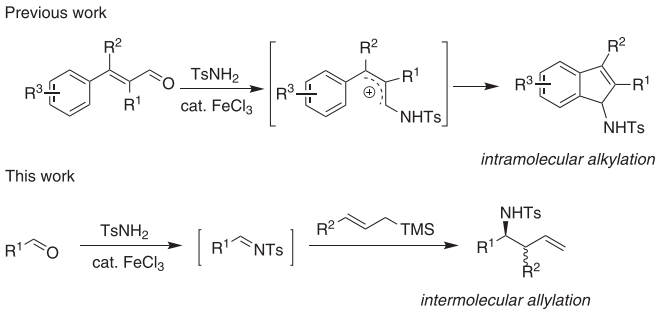
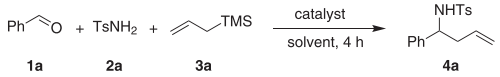


Scheme 1. Strategies for iron-catalyzed intramolecular and intermolecular reactions.

Table 1. Optimization of reaction conditions[a]



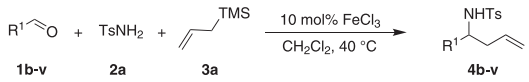
1a 2a 3a 4a

Entry	Catalyst (mol%)	Solvent	Temperature (°C)	Yield (%)[b]
1	$FeCl_3$ (5)	CH_2Cl_2	rt	53
2	$FeCl_3$ (5)	CH_2Cl_2	40	81
3	$FeCl_3$ (10)	CH_2Cl_2	40	94
4	$FeCl_3$ (15)	CH_2Cl_2	40	80
5	$FeCl_3$ (10)	MeCN	40	28
6	$FeCl_3$ (10)	Dichloroethane	80	89
7	$FeCl_3$ (10)	THF	60	Trace
8	$FeCl_3$ (10)	CH_3NO_2	40	64
9	$FeCl_3$ (10)	DMF	80	0
10	$FeCl_3$ (10)	DMSO	80	0
11	$FeCl_3$ (10)	Benzene	80	78
12	$FeCl_3$ (10)	EtOH	75	Trace
13	$FeCl_3 \cdot 6H_2O$ (10)	CH_2Cl_2	40	77
14	$FeCl_2$ (10)	CH_2Cl_2	40	31
15	$Fe(NO_3)_3 \cdot 9H_2O$ (10)	CH_2Cl_2	40	74
16	$Fe(ClO_4)_3 \cdot H_2O$ (10)	CH_2Cl_2	40	43
17	$Fe(acac)_3$ (10)	CH_2Cl_2	40	0
18	$TiCl_4$ (10)	CH_2Cl_2	40	0
19	$ZnCl_2$ (10)	CH_2Cl_2	40	64
20	CuI (10)	CH_2Cl_2	40	0
21	—	CH_2Cl_2	40	0
22	TfOH (10)	CH_2Cl_2	40	Trace

[a]Reaction conditions: benzaldehyde (**1a**, 1.0 mmol), $TsNH_2$ (**2a**, 1.5 mmol), allyltrimethylsilane (**3a**, 1.3 mmol), solvent (5.0 ml), in air.
[b]Isolated yield.

optimized reaction conditions show good substrate compatibility with a wide variety of aromatic and allylic aldehydes, providing the corresponding homoallylamine derivatives in good to excellent yields (Table 2, entries 1–19). Aliphatic aldehydes such as propanal do not undergo this transformation even under harsh reaction conditions (Table 2, entry 21), which results in an intractable mixture. Functional groups, e.g. aromatic methoxy, C=C double bond, cyano and acetal, tolerate the reaction conditions very well (Table 2, entries 5, 6, 11 and 15). With respect to the electronic effect, the substituents on the phenyl ring of benzylic aldehydes have an obvious influence on the product yields. Overall, the reaction is facilitated with electron-rich substrates which bear an electron-donating group on the phenyl ring (Table 2, entries 1–4). The relatively lower

Table 2. Reactions of **2a** and **3a** with various aldehydes[a]



1b-v 2a 3a 4b-v

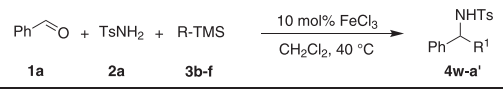
Entry	R^1	Time (h)	Product	Yield (%)[b]
1	2-MeC_6H_4	4	**4b**	91
2	3-MeC_6H_4	4	**4c**	89
3	4-MeC_6H_4	4	**4d**	93
4	2-$MeOC_6H_4$	5	**4e**	96
5	4-$MeOC_6H_4$	5	**4f**	76
6	3,4-$(OCH_2O)C_6H_3$	7	**4g**	67
7	4-FC_6H_4	5	**4h**	73
8	4-ClC_6H_4	5	**4i**	79
9	3-ClC_6H_4	5	**4j**	83
10	2-BrC_6H_4	5	**4k**	75
11	4-CNC_6H_4	5	**4l**	70
12	4-$CF_3C_6H_4$	5	**4m**	82
13	1-Naphthyl	5	**4n**	81
14	2-Naphthyl	5	**4o**	86
15	(*E*)-PhCH=CH	6	**4p**	85
16	(*E*)-PhCH=CBr	6	**4q**	71
17	(*E*)-4-MePhCH=CH	5	**4r**	82
18	(*E*)-4-ClPhCH=CH	6	**4s**	72
19	(*E*)-3,4-(OCH_2O)PhCH=CH	5	**4t**	62
20	(*E*)-PhCH=C(CH_3)	4	**4u**	82[c]
21	CH_3CH_2	6	**4v**	'Mess'

[a]Reaction conditions: aldehydes (**1b–v**, 1.0 mmol), $TsNH_2$ (**2a**, 1.5 mmol), allyltrimethylsilane (**3a**, 1.3 mmol), solvent (5.0 ml), in air.
[b]Isolated yield.
[c]Yield of cyclization product.

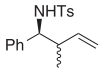
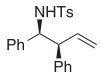
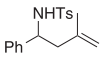
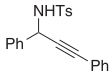
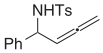
yields of **4f** and **4 g** are presumably due to their lower stability under the iron catalytic conditions (Table 2, entries 5 and 6).[10a,12] Note that when α-alkylated cinnamylaldehyde **1u** is subjected to this reaction, a cyclization product **4u** is obtained exclusively without observation of the sulfonamidoallylation product (Table 2, entry 20). This result is consistent with our previous study in which α-alkylated cinnamylaldehyde was found to be favorable for intramolecular alkylation.[9] In addition, aromatic and cinnamic ketones such as acetophenone and (*E*)-4-phenylbut-3-en-2-one are also found to be unsuitable substrates for this reaction, which might be attributed to the lower electrophilicity of ketone.

To learn about the effect of silyl reagents, we next examined the reaction of **1a** and **2a** with other silyl nucleophiles (Table 3). The substituents of the allylsilanes have obvious influences on the reaction outcomes. With the β-substituted allylsilane **3d**, the reaction can be accomplished at room temperature with a full conversion of **1a**; while the reactions of γ-substituted allylsilanes **3b** and **3c** proceed slowly at 40 °C to give the corresponding homoallylamines **4w** and **4x** in excellent *syn* diastereoselectivity, accompanied by a small amount of unreacted **1a**. Based on previous experimental and theoretical studies,[13] this higher stereoselectivity can probably be explained by the hypothesis that the reaction may take place through antiperiplanar transition states **5a** and **5b** (Fig. 1). The γ-substituted allylsilane prefers to react with the imine through transition state **5a** to produce the *syn* product, in which the steric interaction between the imine substituent and the vinyl substituent of the allylsilane is reduced; on the contrary, disfavored transition state **5b** will lead to the *anti* isomer. More bulky phenyl-substituted allylsilane **3c**

Table 3. Reactions of **1a** and **2a** with various silyl nucleophiles[a]

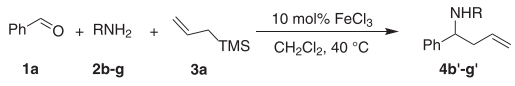


1a 2a 3b-f 4w-a'

Entry	R		Time (h)	Product		Yield (%)[b]
1	(*E*)-$CH_3CH{=}CHCH_2$	**3b**	24		**4w**	81[c]
2	(*E*)-$PhCH{=}CHCH_2$	**3c**	24		**4x**	61
3[d,e]	$CH_2{=}C(CH_3)CH_2$	**3d**	18		**4y**	69
4[e]	Phenylethynyl	**3e**	24		**4z**	0
5[d]	Propargyl	**3f**	2		**4a′**	'Mess'

[a]Reaction conditions: benzaldehyde (**1a**, 1.0 mmol), $TsNH_2$ (**2a**, 1.5 mmol), allylsilanes (**3b–f**, 1.3 mmol), solvent (5.0 ml), in air.
[b]Isolated yield.
[c]Mixture of *syn* and *anti* isomers; *syn*/*anti* = 10:1.
[d]Room temperature.
[e]R^1=R.

Table 4. Examination of other amine sources[a]



1a 2b-g 3a 4b'-g'

Entry	R	Time (h)	Product	Yield (%)[b]
1	$PhSO_2$ (**2b**)	4	**4b′**	91
2	2-$MePhSO_2$ (**2c**)	4	**4c′**	90
3	4-$ClPhSO_2$ (**2d**)	4	**4d′**	87
4	CH_3SO_2 (**2e**)	4	**4e′**	72
5	$PhCH_2OCO$ (Cbz, **2f**)	12	**4f′**	0
6	$(CH_3)_3COCO$ (Boc, **2 g**)	12	**4g′**	0

[a]Reaction conditions: benzaldehyde (**1a**, 1.0 mmol), RNH_2 (**2b–g**, 1.5 mmol), allyltrimethylsilane (**3a**, 1.3 mmol), solvent (5.0 ml), in air.
[b]Isolated yield.

undergoes this reaction exclusively through transition state **5a** that results in the formation of the *syn* diastereomer solely. To our disappointment, alkynylsilane **3e** and propargylsilane **3 f** fail to give the desired products. Compound **3e** remains intact under the employed reaction conditions, while use of **3 f** leads to an intractable mixture with full consumption of **1a** and **3 f**.

To further investigate the generality of this reaction, several other sulfonamides and carbamates such as benzenesulfonamide (**2b**), 2-methylbenzenesulfonamide (**2c**), 4-chlorobenzenesulfonamide (**2d**), methanesulfonamide (**2e**), benzyl carbamate (**2f**) and *tert*-butyl carbamate (**2 g**) were examined in this reaction (Table 4). Under the optimal reaction conditions, **2b–e** react smoothly with **1a** and **3a** to give the corresponding sulfonamidoallylation products **4b′**–**e′** in good to excellent yields. However, **2f** and **2 g** are found to be unsuitable reaction partners: no reactions are observed even under harsh reaction conditions.

Finally, removal of the tosyl group was tested. Product **4a** was successfully detosylated under reductive conditions (Na/naphthalene) to afford the deprotection homoallylamine in 64% yield.

With the aim of understanding the mechanism, several control experiments were conducted (Scheme 2). First, prior-prepared aldimine **5c** was reacted with allyltrimethylsilane under the optimal conditions in air. After 3 h, 95% yield of allylation product **4a** is obtained; without $FeCl_3$, the reaction does not occur. In the presence of Brønsted acids (e.g. TfOH and HCl, 10 mol%), most of **5c** is decomposed into **1a** without the formation of **4a**. Interestingly, upon the reaction of **5c** with allyltrimethylsilane under the catalysis of $FeCl_3$, we also find that part of **5c** is decomposed into **1a** and **2a** at the beginning of the reaction; however, they disappear when the reaction is finished (monitored using TLC, 3 h). Second, on conducting the model reaction under argon atmosphere with 10 mol% $FeCl_3$, only 37% yield of **4a** is obtained after 8 h at 40 °C, which can be markedly improved to 91% yield when a small amount of water is added (15 μl, 4 h). Third, a three-component reaction was carried out involving **1a** with allyltrimethylsilane for 1 h under the catalysis of $FeCl_3$, then $TsNH_2$ was added. Under these reaction conditions, only a trace amount of **4a** is observed without the formation of homoallylic alcohol. Fourth, reaction of **1a** (1.0 equiv.) with **2a** (1.5 equiv.) for 1 h under the catalysis of 10 mol% $FeCl_3$ affords 34% yield of aldimine **5c** along with unreacted **1a** and **2a**. These experiments reveal that this reaction involves the equilibrium formation of a sulfonylimine, which, rather than homoallylic alcohol, functions as the intermediate;[10a,14] the addition of an allyltrimethylsilane shifts the equilibrium towards the formation of a homoallylamine derivative; and the reaction is assisted by both $FeCl_3$ and water.[15]

Based on the above results, a tentative reaction pathway is proposed, as shown in Scheme 3. The first step is the nucleophilic addition of a sulfonamide to the carbonyl group of the

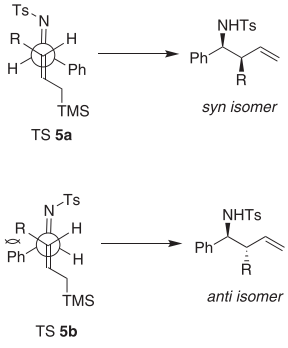
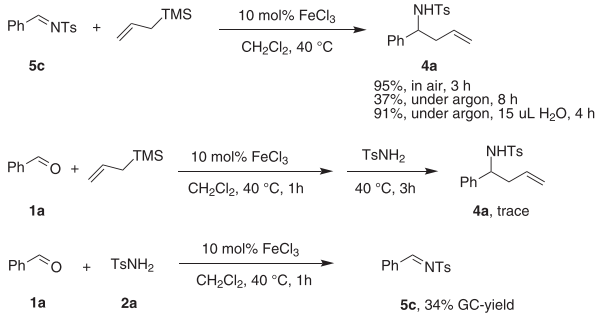
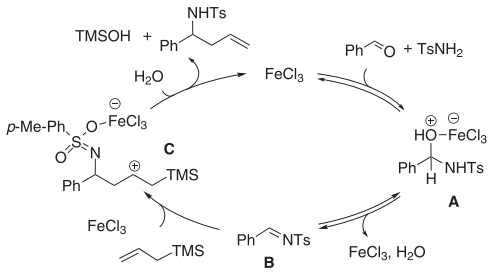


Figure 1. Antiperiplanar transition states (TSs) **5a** and **5b**.



Scheme 2. Control experiments.



Scheme 3. Tentative reaction pathway.

aldehyde with the aid of $FeCl_3$ to give the intermediate **A**, which then loses $FeCl_3$ and water to afford the sulfonylimine **B**. This process is reversible. Subsequently, activation of sulfonylimine **B** by $FeCl_3$ followed by addition of allylsilane leads to a silyl-stabilized carbocation **C**, which, after loss of the trimethylsilyl group in the presence of water, would give rise to the corresponding homoallylamine derivative.

Conclusions

In summary, a mild, economical and environmentally benign three-component sulfonamidoallylation reaction between aldehydes, sulfonamides and allylsilanes for the synthesis of homoallylamine derivatives has been achieved. The major advantages of this method include: (i) using cheap and ecologically benign $FeCl_3$ as the catalyst; (ii) construction of a C–N bond and a C–C bond in a one-pot procedure without advance preparation of unstable aldimines; (iii) carrying out the reaction in air atmosphere without additional anhydrous conditions; and (iv) excellent *syn* stereoselectivity with γ-substituted allylsilanes. In addition, catalytic three-component amidoallylation reactions involving *in situ* formed sulfonylimines and allylsilanes have not been systematically explored previously. The method described can serve as a supplement to existing methodologies. Further refining this method in organic synthesis is underway in our laboratory.

Experimental

To a solution of aldehyde (1 mmol, 1.0 equiv.) in CH_2Cl_2 (5 ml) were added sulfonamide (1.5 equiv.) and $FeCl_3$ (10 mol%, 98% purity; purchased from Alfa Aesar). The resulting mixture was stirred at 40 °C for 1 h, and then allyltrimethylsilane (1.3 equiv.) was added. The mixture was further stirred at 40 °C until the aldehyde was completely consumed (monitored using TLC). After that, 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 Na_2SO_4 and concentrated. The crude product was purified by column chromatography on silica gel with a mixture of petroleum ether and ethyl acetate (10:1) to afford the corresponding product. Note that when allyltrimethylsilane was successively added to the reaction mixture, a lower yield of **4a** was obtained (77%). See the supporting information for details.

Acknowledgments

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