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Organometallic Chemistry

Transition-Metal Free Electrophilic Aminations of Polyfunctional *O*-2,4,6-Trimethylbenzoyl Hydroxylamines with Zinc and Magnesium Organometallics

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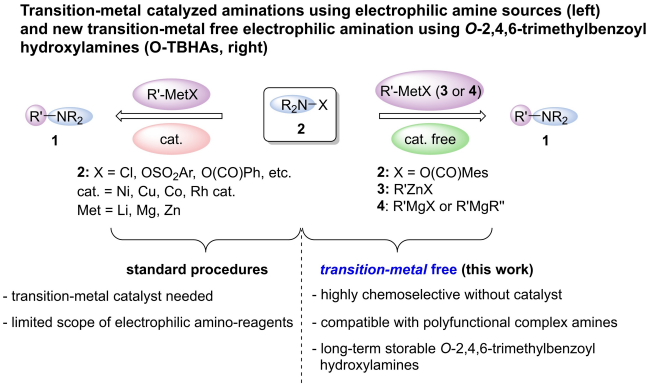
Abstract: We reported a new electrophilic amination of various primary, secondary and tertiary alkyl, benzylic, allylic zinc and magnesium organometallics with *O*-2,4,6-trimethylbenzoyl hydroxylamines (O-TBHAs) in 52–99 % yield. These O-TBHAs displayed an excellent long-term stability and were readily prepared from various highly functionalized secondary amines via a convenient 3 step procedure. The amination reactions showed remarkable chemoselectivity proceeding without any transition-metal catalyst and were usually complete after 1–3 h reaction time at 25 °C. Furthermore, this electrophilic amination also provided access to enantioenriched tertiary amines (up to 88 % *ee*) by using optically enriched secondary alkylmagnesium reagents of the type *s*-AlkylMgCH$_2$SiMe$_3$.

Polyfunctional amines are ubiquitous structural units present in many pharmaceutical drugs.[1] Thus, the preparation of highly functionalized amines (**1**) is central in organic synthesis. Although nucleophilic substitutions using nitrogen nucleophiles on haloalkanes are considered standard preparations of amines, the construction of complex amines by this method is strongly limited.[2] In fact, only a small percentage of such reactions can be performed using non-activated secondary (<6 %) or tertiary (<1 %) haloalkanes.[2] Thus, complementary electrophilic substitution reactions involving electrophilic amino-reagents of type X–NR$_2$ (**2**) where X is a leaving group, have become a more and more important alternative for preparing complex tertiary amines of type **1** (Scheme 1, left). Pioneering work of Erdik[3] and Narasaka[4] was extended by transition-metal catalyzed electrophilic aminations reported by Johnson[5] and Wang[6] using Ni- or Cu-catalysts.[7] A Co-catalyzed[8] variant has also been demonstrated. However, the main drawback of such reactions is the requirement of using instable or difficult to prepare electrophilic reagents of the type X–NR$_2$ (**2**: X = Cl, OSO$_2$Ar, OSO$_2$Me)[9] as well as the need of expensive and toxic transition metal catalysts. Sparked by a continuous flow amination using aryllithiums,[10] we have envisioned a general and reliable procedure using relatively stable and easy to prepare electrophilic amination reagents derived from *O*-2,4,6-trimethylbenzoyl hydroxylamines (O-TBHAs) of type **2**, with readily available zinc and magnesium reagents[11] of type **3** and **4** (Scheme 1, right). Herein, we report such a transition-metal free amination involving various alkyl- and benzylic or allylic zinc reagents as well as alkylmagnesium halides and readily prepared new and pharmaceutically relevant O-TBHAs. Furthermore, this method has been extended to the preparation of highly optically enriched tertiary alkyl amines using chiral *s*-alkylmagnesium reagents of type *s*-AlkylMgCH$_2$SiMe$_3$.[12]

In preliminary experiments, we have focused our attention on the nature of the electrophilic amination reagent. After testing various *O*-acyl hydroxylamines,[13] we have found that *O*-2,4,6-trimethylbenzoyl hydroxylamines



Scheme 1. Electrophilic amination reactions of alkylzinc and -magnesium reagents of type **3** and **4** and amino-reagents of type **2** leading to tertiary amines of type **1**.

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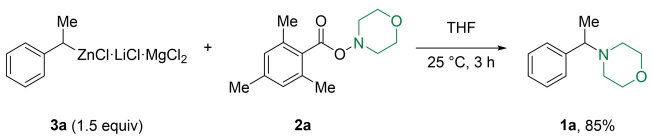
(O-TBHA) such as **2a** gave superior results compared to other *O*-acyl hydroxylamine derivatives. More importantly, these new reagents proved to be long-term storable for several months as solids at 0 °C in the refrigerator and were clearly the reagents of choice.[13] Thus, the reaction of **2a** (1.0 equiv) with α-methylbenzylzinc chloride (**3a**, 1.5 equiv) in THF at 25 °C for 3 h gave the desired amine **1a** in 85 % isolated yield (Scheme 2). Interestingly, a conventional nucleophilic substitution reaction of α-methylbenzyl chloride with morpholino amide did not give the desired product.[13]

With these results in hand, we developed a robust, practical and scalable preparation for these new O-TBHAs of type **2** adapting the original procedure of O'Neil.[8c,12,14] Thus, a range of various secondary amines R^1R^2N–H (**5**) including complex drug molecules were treated with an excess of acrylonitrile (5 equiv, MeOH, 55 °C, 2 h) leading to the 2-cyanoethylamines **6**.[13] These amines were oxidized to the corresponding amine *N*-oxides with *m*CPBA (*meta*-chloroperoxybenzoic acid) in CH_2Cl_2 (−78 °C to 25 °C, 4 h). After a Cope elimination,[14] hydroxylamines (**7**) were obtained in ca. 70 % yield. Finally, protection of **7** with mesityloyl chloride gave the O-TBHAs of type **2** in 52–86 % overall yield. These electrophilic amination reagents are mostly white solids or in some cases viscous oils which were stored for months in a refrigerator without decomposition (at 0 °C). Importantly, a broad scope of secondary alkyl amines were used bearing various functionalities and remarkably a number of pharmaceutically relevant amines proved to be well compatible with this improved procedure (Scheme 3).

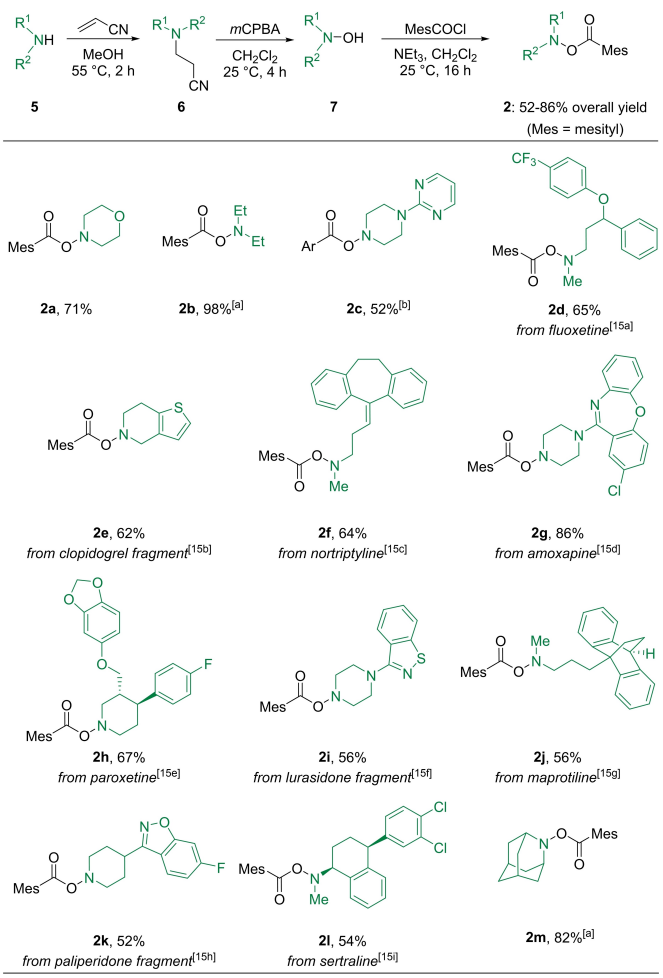
With this convenient access to O-TBHAs of type **2** in our hands, we turned our attention to the nature of the zinc reagent and to the presence of additional metallic salts. Thus, we prepared a range of octylzinc derivatives[16] (**3b–i**) as shown in Table 1 and reacted them with O-TBHA **2b**. To our surprise, we found that the presence of iodide or bromide anions in the zinc reagent had a deleterious effect.[17] Whereas the presence of chloride ions did not hamper the amination reaction. Thus, with reagent $OctZnCl{\cdot}LiCl{\cdot}MgCl_2$ (**3f**) which was conveniently prepared by treating octyl chloride with Mg turnings (2.5 equiv) in the presence of LiCl (1.25 equiv) and $ZnCl_2$ (1.1 equiv)[16c] the amination proceeded smoothly and afforded *N*,*N*-diethyloctylamine **1b** in 67 % isolated yield.

We have found that alkylzinc reagents as well as benzylic and allylic zinc species were excellent substrates (Scheme 4). Thus, we have prepared 4-phenyl-3-butenylzinc chloride (**3j**) from the corresponding alkyl chloride using Mg, LiCl, $ZnCl_2$ as described above (in ca. 50 % yield).[16c] Reaction of **3j** with O-TBHAs **2d** and **2f** (THF, 25 °C, 3 h) gave the desired amines **1c–d** in 80–84 % yield. Interestingly, although iodide ions were usually not tolerated,[13] $(CF_3CH_2)_2Zn$ (**3k**) was prepared from CF_3CH_2I and Mg, LiCl and $ZnCl_2$ (0.5 equiv)[18] and gave excellent results



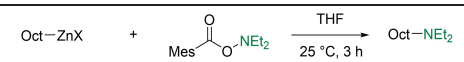
3a (1.5 equiv) **2a** **1a**, 85%

Scheme 2. Electrophilic amination of α-methylbenzylzinc chloride **3a** with morpholino 2,4,6-trimethylbenzoate **2a**.



Scheme 3. Scope of O-TBHAs of type **2**. Yields refer to isolated analytically pure products. [a] Commercially available hydroxylamines were used. [b] 2,6-Dichlorobenzoyl chloride was used instead of mesityloyl chloride, Ar = 2,6-dichlorobenzoyl.

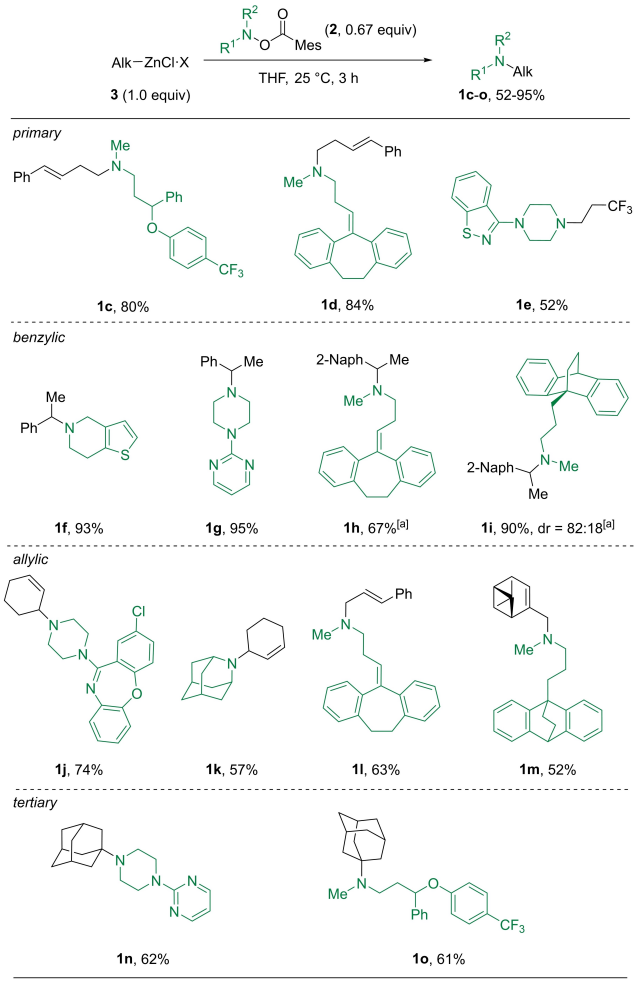
Table 1: Optimization of alkylzinc reagent.



3b-i (1.5 equiv) **2b** **1b**

Entry	Zinc reagent	Yield of amine [%][a]
1	Oct–ZnI (**3b**)	0
2	Oct–ZnI·LiCl (**3c**)	0
3	Oct–ZnCl·MgBrCl (**3d**)	< 5
4	Oct–ZnCl·LiCl·MgBrCl (**3e**)	< 5
5	Oct–ZnCl·LiCl·$MgCl_2$ (**3f**)	67[b]
6	Oct_2Zn (**3g**)	19
7	Oct_2Zn·LiCl (**3h**)	23
8	Oct_2Zn·LiCl·MgBrCl (**3i**)	32

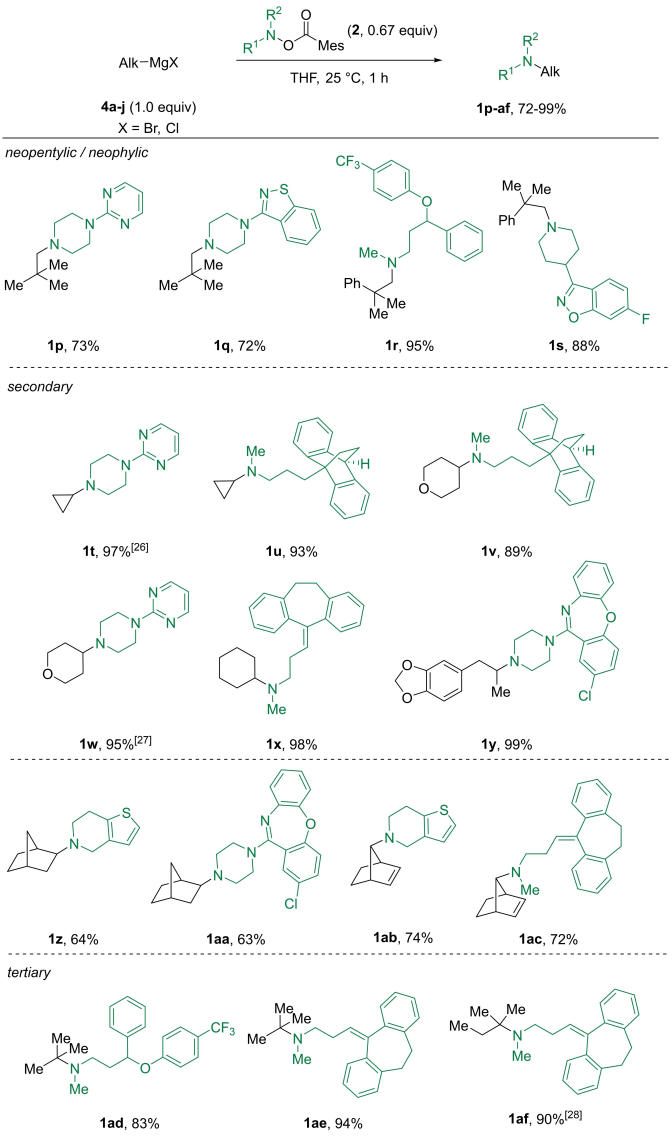
[a] All reactions were performed on 0.5 mmol scale. Yields were determined by GC-analysis using undecane as internal standard. [b] Isolated yield of analytically pure product.



Scheme 4. Electrophilic aminations of alkylzinc reagents of type **3** with O-TBHAs of type **2** leading to tertiary alkyl amines of type **1**. X = Cl·MgCl$_2$·LiCl, Cl·MgBrCl·LiCl, LiCl or Cl·MgICl·LiCl. Yields refer to isolated analytically pure products. [a] 2-Naph = 2-naphtyl.

when treated with **2i** leading to the heterocyclic amine **1e** in 52 % yield. Next, we focused our attention on the preparation of α-substituted benzylic amines which are not accessible by a standard nucleophilic substitution due to competitive elimination.[2,13] Since benzylic zinc reagents are readily prepared[19] we have used them in this electrophilic amination producing several α-methyl substituted benzylic amines **1f–i** in 67–95 % yield. Finally, we have examined allylic zinc reagents (available from the corresponding allylic chlorides).[20] In the case of 2-cyclohexenylzinc chloride (**3m**) smooth allylations with O-TBHA **2g** and **2m** produced the expected amines **1j** and **1k** in 57–74 % yield. Interestingly, in the case of non-symmetrical allylic zinc reagents such as cinnamylzinc chloride[20] and myrtenylzinc chloride,[20] the new C–N bond was exclusively formed from the least substituted end of the allylic system producing the allylic amines **1l** and **1m** in 52–68 % yield. Also, we have successfully treated adamantylzinc chloride prepared from adamantyl bromide[21] with the electrophilic amines **2c–d** and obtained the α-tertiary *N*-adamantylamines **1n** and **1o** in 61–62 % yield.

Then, we have examined organomagnesium reagents of type **4** and especially emphasizing the preparation of amines inaccessible by conventional nucleophilic substitutions (Scheme 5). Thus, neopentylic moieties (and neophylic ($PhMe_2CCH_2$) groups) are especially reluctant to be introduced by nucleophilic substitutions.[2a] However, the treatment of readily prepared neopentylmagnesium bromide (**4a**, tBuCH$_2$MgBr)[22] with O-TBHAs **2c** and **2i** in THF (25 °C, 1 h) produced the desired amines **1p–q** in 72–73 % yield. Similarly, neophylmagnesium chloride (**4b**, $PhMe_2CCH_2MgCl$)[23] reacted with the amination reagents **2d** and **2k** providing, under the same conditions, the tertiary amines **1r–s** in 88–95 % yield. Secondary alkylmagnesium halides were also excellent substrates and their reactions



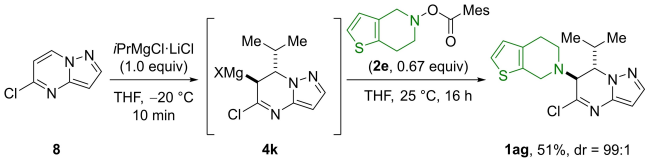
Scheme 5. Electrophilic aminations of various alkylmagnesium reagents of type **4** with O-TBHAs of type **2** leading to products of type **1**. Yields refer to isolated analytically pure products.

with various O-TBHAs **2c**, **2f–g**, **2j** gave the desired amines **1t–y** in 89–99 % yield. Diastereoselective aminations may be performed using *exo*-norbornylmagnesium bromide (**4g**, *exo*:*endo* = 3:1) prepared by the reacting of Mg turnings with *exo*-norbornyl bromide.[24] After an amination with reagents **2e** and **2g** (0.67 equiv) a mixture of *exo*- and *endo*-norbornylamines **1z–aa** were obtained (dr = 3:1), which could be isolated as single *exo*-diastereoisomers in 63–64 % yield (dr = 99:1). Also, *syn*-7-norbornenylmagnesium bromide[25] (**4h**) reacted with retention of configuration with O-TBHA **2e** and **2f** providing the complex tertiary amines **1ab–ac** in 72–74 % yield (dr > 99:1). Finally, tertiary alkylmagnesium chlorides like *t*-BuMgCl (**4i**) and $EtMe_2CMgCl$ (**4j**) readily underwent the amination reaction with **2d** and **2f** leading to the amines **1ad–af** in 83–94 % yield.

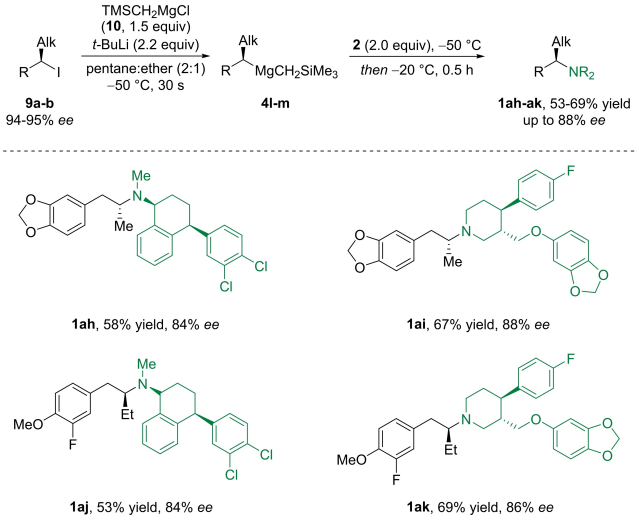
Recently, we have reported the nucleophilic addition of *i*PrMgCl·LiCl to pyrazolo[1,5-*a*]pyrimidine **8** leading to the *trans*-organomagnesium derivative **4k**.[29] Treatment of this magnesium species with O-TBHA **2e** at 25 °C for 16 h gave the heterocyclic amine **1ag** in 51 % yield (dr = 99:1; Scheme 6).

Next, we turned our attention to the preparation of enantioenriched tertiary amines. Recently, we have shown that a Barbier procedure allowed to convert various secondary alkyl iodides **9a–b** to the corresponding Grignard reagents **4l–m** by the reaction of **9a–b** in the presence of trimethylsilylmethylmagnesium chloride (**10**) with *t*-BuLi at −50 °C for 30 s.[12] Treatment of these mixed Grignard species **4l–m** with complex O-TBHA (**2h**, **2l**) at −20 °C for 30 min gave the desired amines **1ah–ak** with high retention of configuration[30] (Scheme 7).

In summary, we have reported a broadly applicable electrophilic amination reaction leading to a range of polyfunctional tertiary alkyl amines including enantioenriched amines (up to 88 % *ee*). In strong contrast to other electrophilic aminations, our method does not require any transition-metal catalysts due to the choice of sterically demanding *O*-2,4,6-trimethylbenzoyl hydroxylamines (O-TBHA) as amination reagents and proceeds at room temperature within a few hours. The method completes nicely the standard nucleophilic amination procedures allowing the straightforward preparation of complex and sterically demanding amines.



Scheme 6. Electrophilic amination of heterocyclic organomagnesium derivative **4k** with O-TBHA **2e**.



Scheme 7. Preparation of enantioenriched tertiary amines. Yields refer to isolated analytically pure products.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the Supporting Information of this article.

Keywords: Amines · Asymmetric Synthesis · Electrophilic Amination · Organomagnesium Reagents · Organozinc Reagents

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[30] The absolute configuration of the obtained products was confirmed by X-ray analysis. See reference [12].

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