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Scandium-Catalyzed *para*-Selective Alkylation of Aromatic Amines with Alkenes

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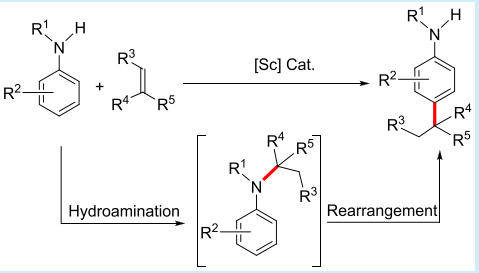
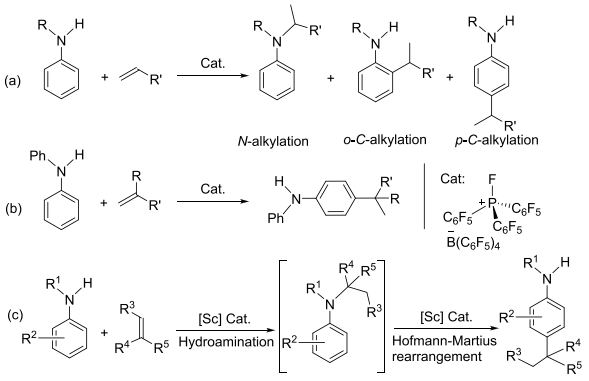
Supporting Information

ABSTRACT: An efficient *para*-alkylation of primary and secondary anilines with a variety of sterically encumbered alkenes using a simple β-diketiminato scandium catalyst is reported. This protocol features 100% atom economy, excellent chemo- and regioselectivity, broad substrate scope, and good functional group tolerance. Mechanistic studies disclosed that the reaction probably proceeded via a tandem hydroamination/Hofmann−Martius rearrangement.



The development of efficient synthetic methodologies for the aromatic amines remains attractive in catalysis research because this class of compounds plays a central role in the fine chemical and pharmaceutical industries.[1,2] To this end, functionalization of aniline and its derivatives using alkenes has emerged and represents an atom- and step-economical method to a variety of alkyl-substituted aromatic amines.[3−5] In this context, transition-metal-catalyzed hydroarylation of alkenes with tertiary anilines has been successfully achieved with high regioselectivity at either *para* or *ortho* positions.[6,7] However, acid- or transition-metal-mediated Friedel−Crafts-type reactions of alkenes with primary/secondary anilines containing reactive N−H groups often result in a mixture of hydroamination (*N*-alkylation) and hydroarylation (*ortho*- and *para*-C-alkylation) products (Scheme 1a).[8] Selective *ortho*-alkylation of primary/secondary anilines has been achieved in a few cases.[9] To date, there is only one precedent for *para*-alkylation of diphenylamine with alkenes by using a main group Lewis acid catalyst via Friedel−Crafts reaction (Scheme 1b).[10] However, substrate scope in this reaction was limited to the sterically bulky diarylamine because the electrophilic phosphonium cation used could be deactivated by the Lewis basic substrate, thus greatly restricting synthetic utility. In our previous study, we designed and synthesized scandium dialkyl complexes based on unsymmetric β-diketiminato ligands that were able to mediate regioselective hydroaminoalkylation of tertiary anilines with a variety of alkenes in combination with a borate compound.[11] In contrast, when such a catalyst system was applied in the reactions of primary/secondary anilines with alkenes, it exclusively afforded *para*-selective C−H alkylation products in high yields with good functional group tolerance (Scheme 1c). Mechanistic studies including isolation of the catalytic intermediate and a series of control experiments revealed that the reaction proceeded via a tandem hydroamination/Hofmann−Martius rearrangement to give a formal *para*-C(sp^2)−H alkylation product. This development is described herein.

Scheme 1. Selected Examples of Catalytic Hydroarylation of Alkenes with Primary/Secondary Anilines



We initiated our study by using β-diketiminato scandium dialkyl complex **1** together with 1 equiv of [$PhNHMe_2$][B(C_6F_5)$_4$] reagent for the reaction of *N*-methylaniline (**2a**) with α-methylstyrene (**3a**) under the same conditions typically applied in our previous case (10 mol % catalyst loading, amine/alkene molar ratio = 1.5:1, toluene, 120 °C).[12] Excitingly, this approach exclusively gave Markovnikov-type *para*-alkylation product **4a** in 91% isolated yield, with no *N*-alkylation or *ortho*-alkylation products detected. Inspired by this intriguing result, hydroarylation of a variety of 1,1-disubstituted alkenes with *N*-methylaniline **2a** was tested, and the results are summarized in Scheme 2. Reactions of *para*- or *meta*-methyl-substituted α-methylstyrene with **2a** selectively

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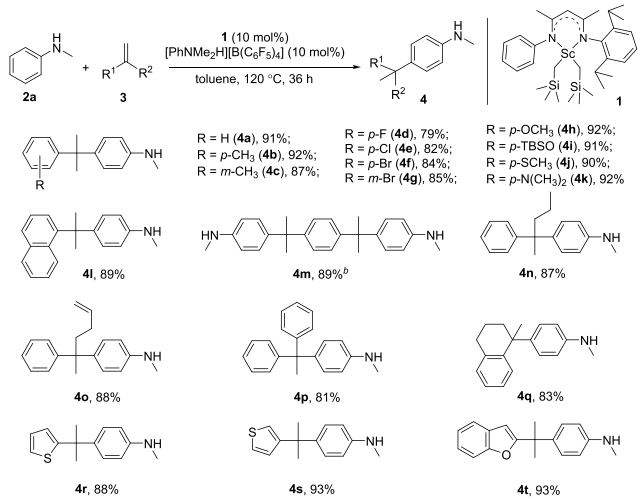
Scheme 2. Scandium-Catalyzed Hydroarylation of 1,1-Disubstituted Alkenes with *N*-Methylaniline[a]

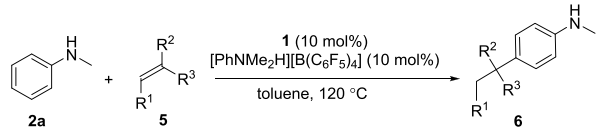


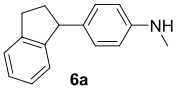
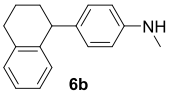
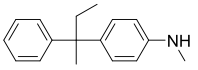
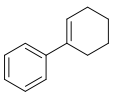
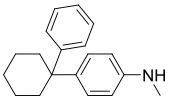
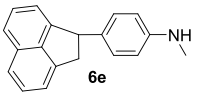
[a]Reaction conditions: *N*-methylaniline **2a** (0.45 mmol), alkenes **3** (0.3 mmol), Sc dialkyl complex **1** (0.03 mmol), $[PhNMe_2H][B(C_6F_5)_4]$ (0.03 mmol), toluene (2 mL), 120 °C, 36 h, isolated yield. [b]**2a** (0.90 mmol).

afforded *para*-alkylation products **4b** and **4c** in 92% and 87% yields, respectively. Remarkably, a variety of α-methylstyrene derivatives containing polar functional groups are tolerated in the reactions. For example, halogen (F, Cl, and Br) substituted alkene substrates are compatible with the catalyst system, giving rise to the corresponding alkylation products **4d**−**4g** with marginally lower isolated yields (79%−85%). α-Methylstyrene with polar electron-donating groups at the *para*-position, such as *t*-butyldimethylsilyloxy (TBSO), methoxy, methylthio, and *N*,*N*-dimethylamino groups, was also suitable for the reactions. The resulting alkylation products **4h**−**4k** were isolated in excellent yields (90%−92%). Transformation of α-isopropenylnaphthalene to **4l** was easily achieved in 89% yield. Double hydroarylation of *para*-disubstituted alkene substrate furnished addition product **4m** when excess *N*-methylaniline reagent was used. When using sterically encumbered α-substituted styrenes as substrates, the reactions still took place, providing access to the *para*-alkylation products **4n**−**4q** with construction of quaternary carbon centers in satisfactory yields (81%−88%). It should be noted that hydroarylation occurred selectively at the C═C double bond that is conjugated with the aromatic ring, with retention of the unconjugated one (i.e., the generation of **4o**). In addition, heterocyclic aromatic olefins containing a thiophene or benzofuran framework are applicable in the present study to form anticipated addition products **4r**−**4t**. However, aliphatic alkenes such as 1-hexene, *trans*-3-hexene, and cyclohexene are not applicable in this hydroarylation reaction. Less sterically hindered aromatic alkene, e.g., styrene, is also precluded for the reaction due to the formation of an oligomer under this catalyst system.[11]

Subsequently, reactions of 1,2-disubstituted and 1,1,2-trisubstituted aromatic alkenes with *N*-methylaniline **2a** were examined under analogous conditions (Table 1). Treatment of indene or 1,2-dihydronaphthalene with **2a** successfully gave *para*-alkylation compounds **6a** (82%) and **6b** (84%), respectively, without other regioisomers being observed. The reactions also proceeded for more sterically crowded

Table 1. Scandium-Catalyzed Hydroarylation of Aromatic Internal Alkenes with *N*-Methylaniline[a]



entry	alkene	product	time (h)	yield (%)
1		 **6a**	24	82
2		 **6b**	24	84
3		 **6c**	36	84
4		 **6d**	48	73
5		 **6e**	48	60

[a]Reaction conditions: *N*-methylaniline **2a** (0.45 mmol), alkenes **5** (0.3 mmol), Sc dialkyl complex **1** (0.03 mmol), $[PhNMe_2H][B(C_6F_5)_4]$ (0.03 mmol), toluene (2 mL), 120 °C, isolated yield.

trisubstituted alkenes to generate **6c** and **6d** with a newly formed quaternary carbon at the *para*-position of *N*-methylaniline, albeit with lower yields (Table 1, entries 3 and 4). Notably, a tricyclic compound with a large π-conjugated system, namely, acenaphthylene, can be facilely hydroarylated by *N*-methylaniline to give the corresponding dearomatizative product **6e** in 60% isolated yield within 48 h. Attempts to extend the substrate scope to tetra-substituted aromatic alkenes failed under our typical conditions probably because of the severe steric hindrances in the alkene.

Given that the scandium dialkyl **1**/$[PhNMe_2H][B(C_6F_5)_4]$ catalytic system exhibited excellent performance in chemo- and regioselective *para*-alkylation of *N*-methylaniline with terminal or internal aromatic alkenes, we next screened aniline substrates under our typical reaction conditions (α-methylstyrene as an alkene coupling partner); the results are summarized in Scheme 3. Substrates with an electron-donating group (methyl) or electron-withdrawing groups (F, Cl, and Br) at the *ortho*-position of *N*-methylaniline were compatible with the reactions, exclusively yielding addition products **7a**−**7d** without noticeably changing the catalytic activity. When increasing the steric hindrance at the nitrogen atom, even with some fused rings, such *para*-alkylation reactions still took place to generate products **7e**−**7j** in high yields. It is remarkable that primary anilines are also involved in this system. For instance, aniline and *o*-chloro-/methoxy-substituted aniline reacted with α-methylstyrene to furnish the *para*-addition products **7k**−**7m** with a 10 mol % catalyst loading. The molecular structure of compound **7m** was further confirmed by single-crystal X-ray diffraction (for details, see

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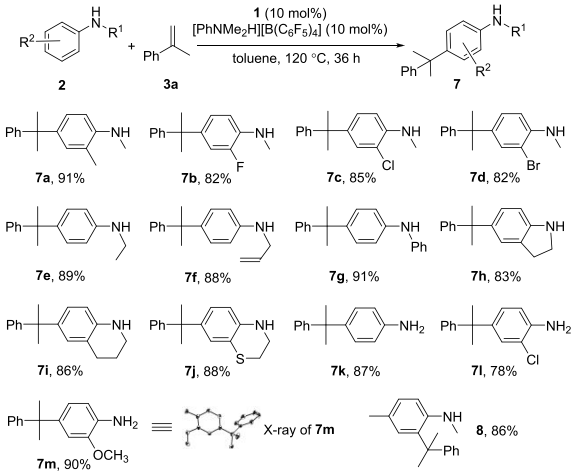
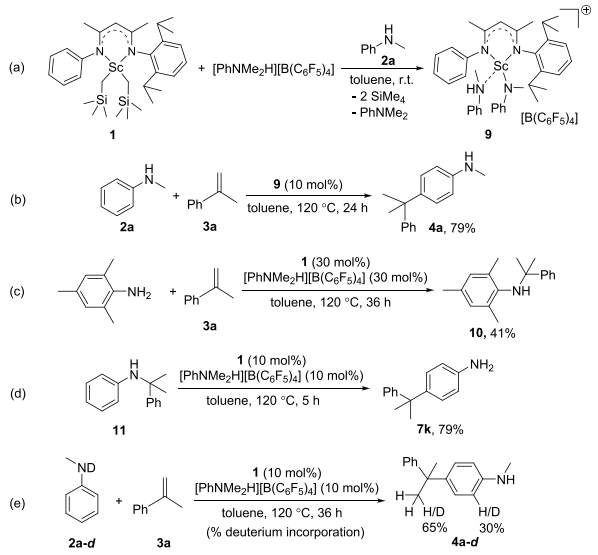
Scheme 3. Scandium-Catalyzed Hydroarylation of α-Methylstyrene with Primary or Secondary Anilines[a]



[a]Reaction conditions: aniline **2** (0.45 mmol), α-methylstyrene **3a** (0.3 mmol), Sc dialkyl complex **1** (0.03 mmol), $[PhNMe_2H][B(C_6F_5)_4]$ (0.03 mmol), toluene (2 mL), 120 °C, 36 h, isolated yield.

Scheme 4. Selected Control Experiments for the Mechanistic Study of the Scandium-Catalyzed *para*-Selective Alkylation Reaction



Supporting Information). In contrast, when using an aniline substrate with a protecting group (e.g., methyl group) at the *para*-position under our standard conditions, hydroarylation still occurred but selectively gave *ortho*-alkylated product **8** in high yield.

It is well-known that rare-earth metal alkyl complexes are prone to protonolysis with primary or secondary amines to form rare-earth amide complexes, which serve as active species for subsequent hydroamination reactions with alkenes to afford *N*-alkylation products.[3,13] It is also well-documented that metal Lewis acids can mediate Hofmann−Martius rearrangement reactions of *N*-alkylated anilines to give the corresponding *ortho*- or *para*-alkylated anilines.[14] Thus, the above scandium-catalyzed *para*-alkylation reaction of primary/secondary anilines might proceed via a tandem hydroamination/Hofmann−Martius rearrangement reaction. Alternatively, classical Friedel−Crafts reaction through electrophilic aromatic substitution could also lead to the same results.[8] To elucidate which pathway is preferred, several control experiments were conducted (Scheme 4). First, the stoichiometric reaction of *in situ* generated cationic scandium alkyl complex[11b] with *N*-methylaniline was investigated. The reaction clearly gave the expected cationic scandium amide complex **9** in 80% isolated yield (Scheme 4a) via protonolysis of the highly reactive Sc−C bond by the N−H group. We found that the coordinated *N*-methylaniline molecule in the complex stabilized the scandium center. When directly applying 10 mol % of complex **9** as a catalyst in the reaction of *N*-methylaniline with α-methylstyrene under standard conditions, it produced *para*-alkylation product **4a** in 79% yield (Scheme 4b), which suggests that scandium amide complex **9** behaved as a catalytic intermediate in the hydroarylation reaction.

Second, the reaction of 2,4,6-trimethylaniline with α-methylstyrene was carried out in the presence of **1**/$[PhNMe_2H][B(C_6F_5)_4]$, which successfully led to the isolation of *N*-alkylation product **10** (Scheme 4c), albeit requiring an increased amount of catalyst loading probably because of severe steric hindrance at the aniline substrate. In addition, we prepared a secondary aniline compound **11**[15] and then treated it under our catalyst system at 120 °C, which resulted in the exclusive formation of *para*-alkylated primary aniline **7k** within 5 h through a rearrangement reaction (Scheme 4d). Apparently, the combination of scandium complex **1** with the borate reagent we employed can serve as an active catalyst for both hydroamination and Hofmann−Martius rearrangement reactions.

Third, a deuterium labeling experiment was also performed to provide more information about the reaction mechanism. The reaction of deuterated *N*-methylaniline (**2a**-*d*) with α-methylstyrene (**3a**) catalyzed by **1**/$[PhNHMe_2][B(C_6F_5)_4]$ gave the *para*-alkylation product **4a**-*d* (Scheme 4e), which showed ca. 65% deuterium incorporation at the newly formed methyl unit as expected. In addition, we also observed 30% deuterium incorporation at the *ortho* position of **4a**-*d*. This is because substrate **2a**-*d* could be partially converted into *ortho*-deuterated *N*-methylaniline under our catalytic system (for details, see Supporting Information). All the above observations indicate that such scandium-catalyzed hydroarylation reaction proceed with a tandem hydroamination/Hofmann−Martius rearrangement mechanism, rather than a classical Friedel−Crafts reaction mechanism. We also propose that highly *para*-selective rearrangement may be caused by both the sterically hindered alkene substrate and the bulky scandium catalyst.

In summary, *para*-selective alkylation of aromatic primary and secondary amine using various sterically demanding alkenes has been achieved by utilization of an easily accessible β-diketiminato scandium dialkyl complex in combination with a borate reagent. The corresponding $C(sp^2)-C(sp^3)$ bond-forming reaction occurred with a 100% atom economy and good functional group tolerance. Remarkably, this protocol showed excellent chemo- and regioselectivity in comparison with widely investigated acid- or transition-metal-catalyzed Friedel−Crafts alkylation reactions.[8] Mechanistic studies disclosed that the resulting *para*-alkylated anilines were formed by an intermolecular hydroamination reaction followed by Hofmann−Martius rearrangement. This study may provide new insights into N−H and C−H functionalization reactions

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promoted by rare-earth catalysts, and further work in this direction is in progress.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.9b03451.

Experimental details, compound characterizations, and X-ray crystallographic data for compound **7m** (PDF)

Accession Codes

CCDC 1956634 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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