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C–H Activation

Triazole-Assisted Ruthenium-Catalyzed C–H Arylation of Aromatic Amides

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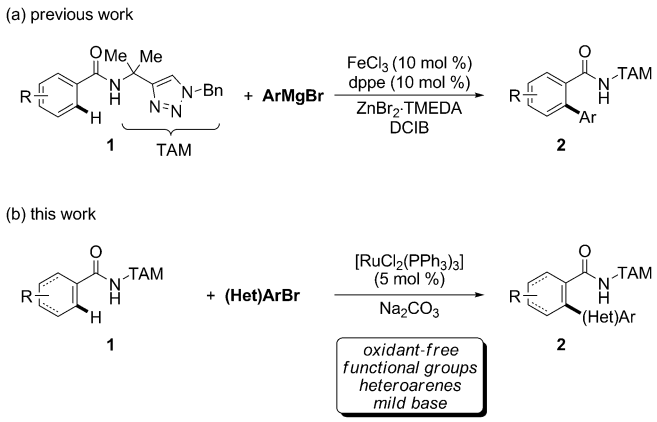
Abstract: Site-selective ruthenium(II)-catalyzed direct arylation of amides was achieved through C–H cleavages with modular auxiliaries, derived from easily accessible 1,2,3-triazoles. The triazolyldimethylmethyl (TAM) bidentate directing group was prepared in a highly modular fashion through copper(I)-catalyzed 1,3-dipolar cycloaddition and allowed for ruthenium-catalyzed C–H arylations on arenes and heteroarenes, as well as alkenes, by using easy-to-handle aryl bromides as the arylating reagents. The triazole-assisted C–H activation strategy was found to be widely applicable, to occur under mild reaction conditions, and the catalytic system was tolerant of important electrophilic functionalities. Notably, the flexible triazole-based auxiliary proved to be a more potent directing group for the optimized ruthenium(II)-catalyzed direct arylations, compared with pyridyl-substituted amides or substrates derived from 8-aminoquinoline.

Introduction

Methods for the activation and subsequent functionalization of otherwise inert C–H bonds are particularly attractive because they avoid the use of prefunctionalized starting materials, and thereby improve the step-economy of the synthetic route.[1] Typical organic substrates contain a variety of C–H bonds with comparable dissociation energies.[1] As a consequence, achieving site selectivity is a prerequisite for the design of synthetically useful C–H-functionalization protocols. Arguably, the most powerful strategies make use of chelation assistance through reversible precoordination.[2] In this context, monodentate Lewis basic entities within the substrate have proven instrumental for advancing the research area of C–H activation. In contrast, Daugulis et al. illustrated the utility of bidentate directing groups derived from 8-aminoquinoline for C–H functionalizations.[3,4] Hence, palladium-[5,6] or copper-catalyzed[7–9] C–H transformations were viable.[10] Chatani et al. very recently reported on useful ruthenium-catalyzed direct C–C formations,[11–13] as well as nickel-catalyzed C–H transformations.[14–16] Likewise, the practical importance of the 8-aminoquinoline directing group was also highlighted by iron-catalyzed direct functionalizations,[17–19] as well as step-economical syntheses of bioactive natural products.[4,20,21]

Despite the remarkable recent advances, this approach is mostly restricted to the 8-aminoisoquinoline, and structural modifications of this auxiliary are particularly challenging in a modular fashion.[4] In consideration of these major limitations, we recently introduced a novel family of highly flexible bidentate directing groups derived from modular 1,2,3-triazoles[22–24] for iron-catalyzed C–H activation.[25] Thus, a triazolyldimethylmethyl (TAM) amide allowed for efficient direct arylations in a site-selective fashion through chelation assistance. Unfortunately, these iron-catalyzed C–H bond transformations were accompanied by the use of an expensive diphosphine ligand, stoichiometric amounts of sacrificial oxidants, as well as highly reactive Grignard reagents as the arylating reagent (Scheme 1 a). Because organomagnesium reagents are required for these C–H functionalizations, valuable electrophilic functional groups were inherently not tolerated by the catalytic system. To address these limitations, we set out to devise com-



Scheme 1. TAM-assisted C–H functionalizations on amides **1** (dppe = 1,2-bis(diphenylphosphino)ethane; TMEDA = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine; DCIB = 1,2-dichloroisobutane).

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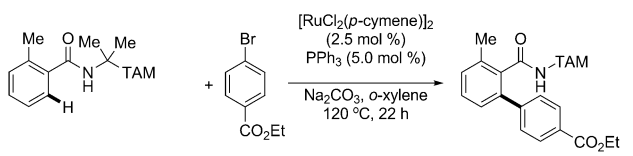
plementary protocols for TAM-assisted C–H activation that would allow for the use of user-friendly organic electrophiles as the arylating reagents and, thus, avoid the use of terminal oxidants. To this end, we developed highly step- and atom-economical ruthenium-catalyzed C–H arylations, with aryl halides,[26–30] of arenes, heteroarenes, and alkenes (Scheme 1 b), reported herein. Notable features of our findings include the use of a highly modular removable triazole-based auxiliary, chemoselective direct arylations with easily accessible aryl bromides, and ample substrate scope.

Results and Discussion

Optimization

We initiated our studies by preparing a representative set of novel benzamides, **1**, displaying substituted 1,2,3-triazoles, by means of the copper-catalyzed 1,3-dipolar Huisgen cycloaddition under mild reaction conditions (see the Supporting Information). With diversely decorated substrates, **1**, in hand, we subsequently probed different reaction conditions for the desired C–H arylation of TAM-amide **1a** with aryl bromide **2a** (Table 1 and Tables S1–S3 in the Supporting Information). Preliminary experiments identified ruthenium(II) complex $[RuCl_2(p\text{-cymene})]_2$ as a highly effective catalyst, particularly when being coordinated by phosphine ligands (Table 1, entries 1–5). However, well-defined ruthenium(II) complex $[RuCl_2(PPh_3)_3]$ outperformed the in situ generated catalytic system (Table 1, entries 1, and 7). Among a variety of bases (K_2CO_3, K_3PO_4, KOAc, NaOAc, or CsOPiv; Piv = pivaloyl), Na_2CO_3 furnished optimal results. Furthermore, *ortho*-xylene allowed for more efficient catalysis compared with reactions being conducted with H_2O[29,31–33] or in toluene, *N*-methyl-2-pyrrolidone (NMP), or DMF as the solvent.

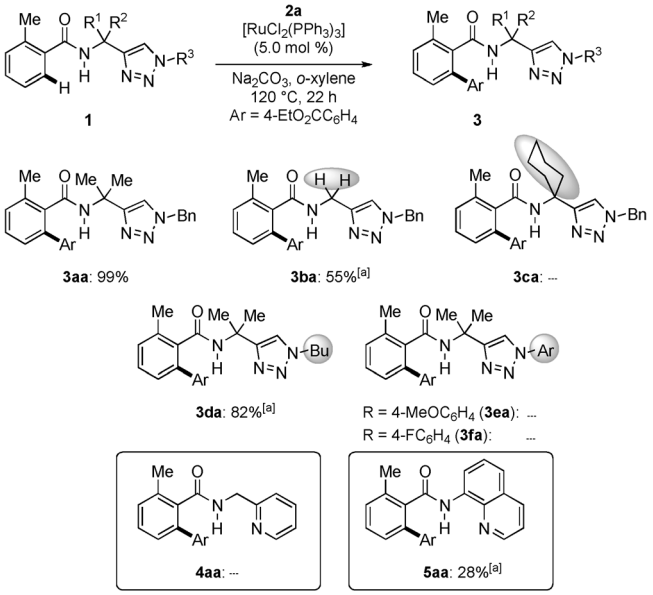
Table 1. Optimization of ruthenium-catalyzed C–H arylation of amide **1a**.[a]



1a 2a 3aa

Entry	Variation from standard conditions	Yield [%]
1	–	98
2	PCy_3, X-Phos, or dppf instead of PPh_3	–
3	HIPrCl instead of PPh_3	–
4	$P(p\text{-Tol})_3$ or $P(4\text{-}FC_6H_4)_3$ instead of PPh_3	86 or 91
5	$[Ru_3(CO)_{12}]$ instead of $[RuCl_2(p\text{-cymene})]_2$	–
6	140 °C	96
7	$[RuCl_2(PPh_3)_3]$ instead of $[RuCl_2(p\text{-cymene})]_2/PPh_3$	99

[a] Reaction conditions: **1a** (0.50 mmol), **2a** (0.60 mmol), base (0.75 mmol), $[RuCl_2(p\text{-cymene})]_2$ (2.5 mol %), catalyst, ligand, *o*-xylene (2.0 mL), 22 h, 120–140 °C. Cy = cyclohexane, dppf = 1,1′-bis(diphenylphosphino)ferrocene; Tol = tolyl.



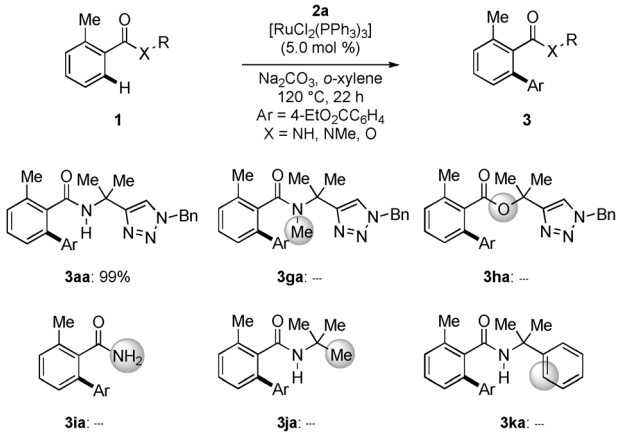
Scheme 2. Variation of the auxiliary substitution pattern. [a] NMR conversion with CH_2Br_2 as internal standard.

With the optimized reaction conditions in hand, we subsequently explored the effect exerted by the substituents of the auxiliary on the performance of the ruthenium catalyst (Scheme 2). A *gem*-dimethyl substitution pattern in the amide backbone of substrate **1a** was found to be beneficial for ensuring high catalytic efficacy (**3aa** versus **3ba** and **3ca**). Moreover, electron-donating N-substituents on the 1,2,3-triazole proved to be suitable, whereas *N*-aryl-substituted derivatives **1e** and **1f** did not deliver the desired products. With these less-electron-donating *N*-aryl substituents on the triazole moiety only the starting materials, **1e** and **1f**, were isolated. It is particularly noteworthy that significantly inferior results were obtained when using the hitherto "gold standard", namely, a pyridyl-substituted amide or the substrate derived from 8-aminoquinoline (**4aa** and **5aa**, respectively). This observation is a strong testament to the superior directing-group power of our triazole auxiliary for ruthenium(II)-catalyzed C–H functionalization.

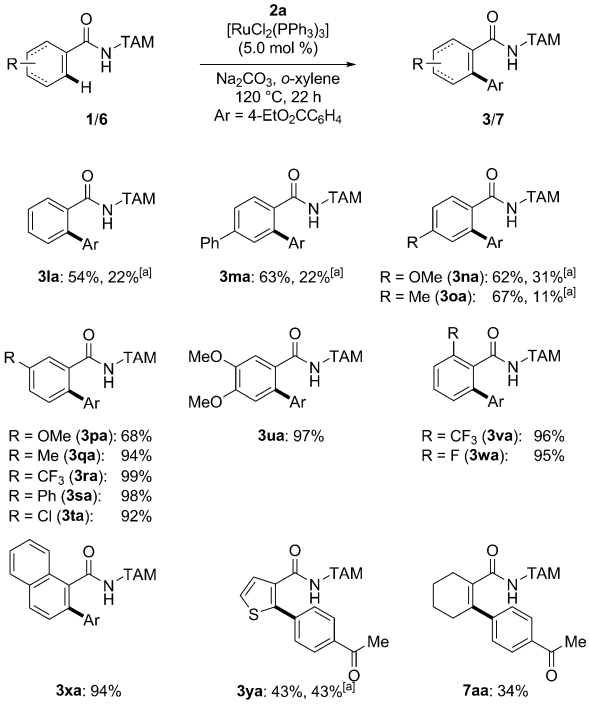
Thereafter, we put the proposed bidentate binding motif of the triazolyl-substituted amides, **1**, to the test (Scheme 3). Tertiary amide **1g** failed to deliver desired arylated product **3ga**, highlighting the importance of the acidic NH-free functionality. In accordance with this finding, the corresponding ester, **1h**, was not a viable substrate for the ruthenium(II)-catalyzed direct arylation. Likewise, simple primary or secondary amides **1i**–**1k**, being devoid of the second Lewis basic nitrogen, were not converted by the ruthenium catalyst.

Scope

Having identified the secondary *N*-benzyl-substituted TAM-amide as the most effective auxiliary, we explored the scope of the ruthenium(II)-catalyzed C–H arylation with diversely decorated substrates **1** (Scheme 4). The direct arylation efficiently proceeded with the parent substrate **1l**, as well as with differ-



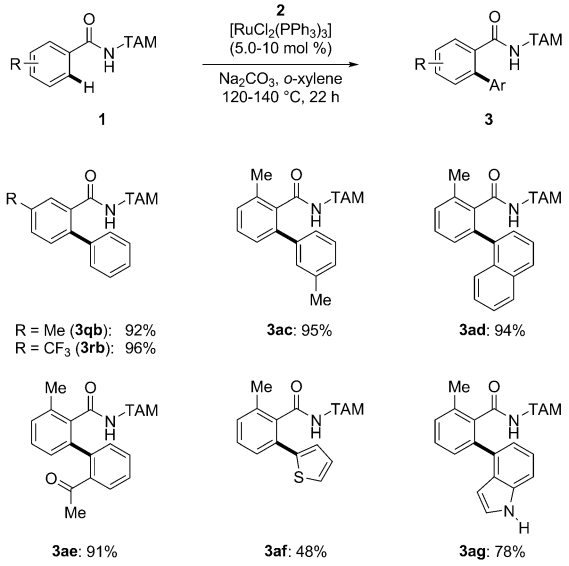
Scheme 3. Evaluation of the bidentate binding motif.



Scheme 4. C–H arylations of (hetero)arenes **1** and alkene **6**. [a] Yield of isolated diarylated product.

ent *para*-substituted amides **1m**–**1o**. Intramolecular competition experiments with *meta*-substituted substrates **1p**–**1u** occurred with excellent site-selectivity at the less-sterically-congested C–H bonds. More-hindered *ortho*-substituted starting materials **1v**–**1x** also delivered the desired products in excellent yields. Notably, the ruthenium(II)-catalyzed C–H activation was not restricted to arenes, but also proved viable to heteroarenes, as well as alkenes, illustrated by the preparation of arylated products **3ya** and **7aa**.

The ruthenium(II) catalyst proved to be widely applicable to C–H bond arylations with a variety of substituted aryl bromides, **2**, (Scheme 5). Indeed, important electrophilic functional groups, such as enolizable ketones, or heteroaromatic moiet-



Scheme 5. Scope of C–H arylation with (hetero)aryl bromides **2**.

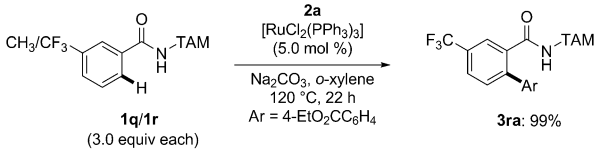
ies, were well tolerated by the catalyst, and electron-deficient, as well as electron-rich, aryl bromides, **2**, were found to be viable electrophiles.[34] For instance, the reaction scope included a thiophene (**3af**) as well as an NH-free indole (**3ag**), which chemoselectively underwent the desired C–H arylation.

Mechanistic Studies

In consideration of the high efficacy of our TAM-assisted ruthenium-catalyzed C–H activation, we conducted mechanistic studies to delineate the mode of action. To this end, direct arylations in the presence of deuterated cosolvents indicated a significant H/D exchange solely occurring in the *ortho*-position of the amide (Scheme S1 and S2 in the Supporting Information), both in the presence and the absence of the organic electrophilic arylating reagent. These findings provided strong support for the elementary step of C–H bond metalation being reversible in nature.

Moreover, intermolecular competition experiments between differently decorated benzamides **1q** and **1r** revealed electron-deficient substrates to be inherently more reactive, thereby exclusively furnishing amide **3ra** as the sole product (Scheme 6). This observation suggests that a simple electrophilic-type arene activation is unlikely to be operating.

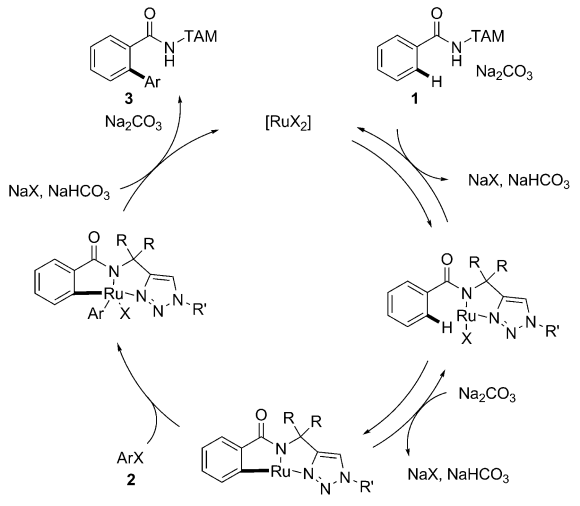
Based on these observations, as well as previous findings,[11,12] we propose the ruthenium-catalyzed C–H arylation to proceed by an initial base-assisted[35] cyclometalation, with



Scheme 6. Intermolecular competition experiment.

a subsequent formal oxidative addition of aryl bromides **2**. The latter might occur by a single-electron transfer (SET)-type process. Finally, reductive elimination and proto-demetalation provide the desired products **3**, and, at the same time, regenerate the catalytically active ruthenium complex (see Scheme 7).

Conclusion



Scheme 7. Proposed catalytic cycle.

In summary, we have disclosed the unprecedented triazole-assisted direct C–H arylation of unactivated amides by ruthenium catalysis. In contrast to the iron-catalyzed C–H-functionalization protocol,[25] the ruthenium(II) catalyst did not require any sacrificial oxidants and was applicable to user-friendly aryl bromides as the arylating reagents. The mild reaction conditions[36] allowed chemoselective C–H arylations of TAM amides in the presence of useful electrophilic functional groups. The TAM auxiliaries were shown to be modular in nature and operated as monoanionic bidentate directing groups, which were removable in a traceless fashion.[25] The triazole auxiliary proved to be superior under the optimized reaction conditions compared with the hitherto-employed bidentate directing groups in C–H activation, that is, amides derived from pyridines or 8-aminoquinoline. Therefore, the ruthenium-catalyzed C–H arylation of benzamides was viable for arenes and alkenes, with excellent chemo-, site- and diastereoselectivity, as well as ample substrate scope.

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Keywords: amides · aryl halides · catalysis · C–H activation · ruthenium · triazoles

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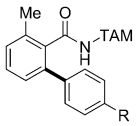
[34] Under otherwise identical reaction conditions (see Scheme 5), ruthenium-catalyzed direct arylations of substrate **1a** with *para*-substituted aryl bromides **2** provided the desired products in high yields:



R = H: 84%
R = CH_3: 91%
R = CF_3: 96%
R = C(O)Me: 96%
R = Cl: 81%
R = NMe_2: 93%

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FULL PAPER

C–H Activation

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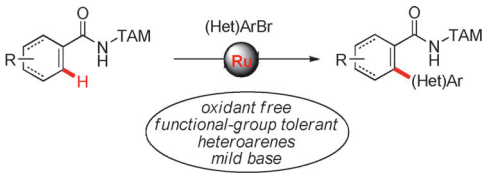
Triazole-Assisted Ruthenium-Catalyzed C–H Arylation of Aromatic Amides



Assisting activation: Ruthenium(II)-catalyzed C–H arylations of (hetero)arenes and alkenes have been achieved with aryl halides through removable bidentate auxiliaries derived from modular 1,2,3-triazoles (see scheme; TAM = triazolyldimethylmethyl).