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Dual Photoredox/Nickel-Catalyzed Regioselective Cross-Coupling of 2-Arylaziridines and Potassium Benzyltrifluoroborates: Synthesis of β-Substitued Amines

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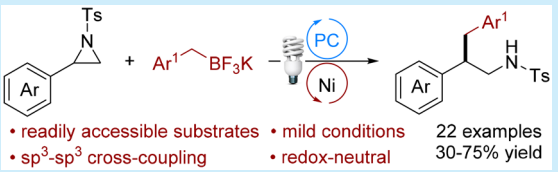
Supporting Information

ABSTRACT: A dual visible light photoredox and nickel-catalyzed cross-coupling reaction of 2-arylaziridines and potassium benzyltrifluoroborates is described for the first time. This strategy features high functional group tolerance, exclusive regioselectivity for reaction at the more hindered C−N bond, easily accessible substrates, and mild redox-neutral reaction conditions. A variety of diversely substituted β-substituted amines are obtained in generally good yields.

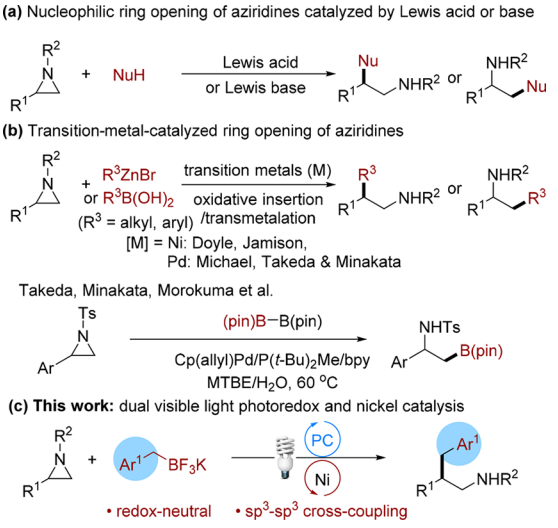


The β-substituted amines are a class of privileged motifs prevalent in many important natural products, pharmaceuticals, agrochemicals, and building blocks in organic synthesis.[1] Accordingly, a great deal of effort has been devoted toward their synthesis. In this context, Lewis-acid- or Lewis-base-catalyzed nucleophilic ring opening of aziridines has been established as one of the most powerful, well-explored, and reliable methods to construct these structures, because of their intrinsic ring strain and ready availability (Scheme 1a).[2,3] Despite tremendous methodological advancements and their advantages, a literature survey revealed that many of them typically suffered from the issue of selectivity during the ring-opening process.[4]

Recently, transition-metal-catalyzed ring opening/cross-coupling of aziridines has proven to be another attractive platform for highly efficient and rapid synthesis of β-disubstituted amines.[5] For instance, Doyle, Sigman, Michael, Minakata, and others reported that nickel and palladium catalysis enabled facile ring opening/cross-coupling of aziridines through a oxidative insertion/tranmetalation process, and the selectivity could be finely controlled by the metals and ligands (Scheme 1b). Employing these strategies, a wide variety of valuable sulfonamide products could be obtained by combination of alkyl and aryl aziridines with suitable coupling partners (e.g., aliphatic organozinc reagents and arylboronic acids). Takeda et al. recently disclosed an elegant Pd-catalyzed regioselective borylation of 2-arylaziridines to provide an efficient approach to β-aminoalkylboronates.[5m] To complement these existing methods, a general and operationally simple strategy with readily available starting materials, high functional group tolerance, and a mild redox-neutral process is still highly desirable.

With the development of visible light photoredox catalysis, merging this mild catalytic strategy with metal catalysis has enabled the design and invention of many unique and significant transformations.[6] Indeed, the dual visible light photoredox/nickel catalysis opened a new fruitful avenue toward development of valuable C−C bond-forming cross-coupling reactions under mild conditions. In these processes, the electronic duality of the excited state of the photocatalyst has always been exploited

Scheme 1. Strategies for Ring Opening of Aziridines



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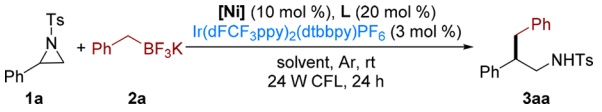
to initiate single electron transfer (SET)-based activation, thus replacing (super)stoichiometric external oxidants or reductants commonly used in traditional metal-catalyzed cross-coupling reactions.[7] Inspired by the pioneering works of Akita[8] on photocatalytic generation of alkyl radicals from readily available and bench-stable potassium alkyltrifluoroborate salts, the group of Molander[9a−h] further established that such a type of reagents could participate in a wide range of dual photoredox/nickel catalytic cross-coupling reactions with various electrophilic halides, enabling assembly of diverse C−C bonds under exceptionally mild conditions. Key to the success of these reactions is the controllable generation of C sp^3 carbon radicals and their subsequent interception by Ni complexes.[9] Inspired by these works and based on our ongoing program on visible light photocatalytic synthesis of nitrogen-containing compounds,[10] we recently launched a research project aimed at inventing a new dual photoredox/nickel catalytic sp^3−sp^3 cross-coupling of aziridines and potassium alkyltrifluoroborates (Scheme 1c).[11] This protocol would provide a mild and redox-neutral approach to the synthesis of β-substituted amines. To our knowledge, there is no precedent for such a transformation.

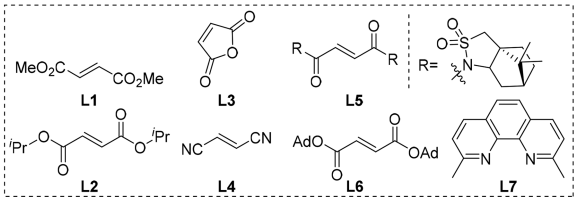
Initially, we chose 2-phenyl-1-tosylaziridine **1a** and potassium benzyltrifluoroborate **2a** as the model substrates using Ir(dFCF$_3$ppy)$_2$(dtbbpy)PF$_6$ as a photocatalyst ($E_{1/2}^{*III/II}$ = +1.21 V vs SCE in MeCN) under irradiation of a 24 W CFL lamp.[12] Pleasingly, it was found that the combination of a range of nickel salts and dimethyl fumarate **L1** as a ligand could indeed promote the desired reaction, giving the β-substituted amine **3aa** in variable yields with the exception of Ni(acac)$_2$ (entries 1 to 4). With NiBr$_2$·glyme as the best candidate (entry 3, 47% yield), we continued to study the effect of solvents and found that dioxane was still the optimal choice (Table 1, entries 3 vs 5,6). Recently, Doyle et al. disclosed that the use of electron-deficient olefin ligands could significantly improve the reaction efficiency in nickel-catalyzed cross-coupling of aziridines by accelerating the reductive elimination step.[5a−d] Thus, we proceeded to investigate a series of other electron-deficient olefin ligands **L2**−**L6** (Table 1, entries 7−11). Surprisingly, the use of sultam-derived fumaramide ligand **L5** and sterically hindered ligand **L6** resulted in a dramatic improvement of reaction efficiency, affording a 60% yield of **3aa** (entries 10 and 11). In contrast, the reaction using bidentate pyridine-derived ligands such as **L7** only resulted in moderate yield (entry 12). Moreover, at a concentration of 0.025 M, the yield of **3aa** could be further increased to 70% (entry 13). Remarkably, the results of a series of control experiments indicated that nickel catalyst, photocatalyst, and visible light were all critical to this cross-coupling reaction (entries 14−16).[13]

Having established the optimal reaction conditions, we first investigated the substrate scope of aziridines. As highlighted in Scheme 2, this dual catalytic system exhibited a broad substrate scope and high functional group compatibility with respect to aziridines. In addition to **1a**, a set of representative aryl *N*-tosylaziridines with either electron-donating (e.g., Me, ^{t}Bu, Ph) or electron-withdrawing substituents (e.g., Cl, F) on the phenyl ring proved to be suitable for the reaction; and the expected products **3ba**−**3ha** were obtained in 37−70% yield. The moderate yield of **3ha** resulted from low conversion of **1h**. Moreover, as shown in the synthesis of **3ea** and **3fa**, aziridines containing sensitive amide and ester functional groups could also be well accommodated. Note that the substitution pattern of the benzene ring has no obvious effect on the cross-coupling. Aziridines **1i**, **1j**, and **1k** with methyl or methoxyl groups at the

Table 1. Condition Optimization[a]



entry	[Ni]	solvent	ligand	yield (%)[b]
1	Ni(cod)$_2$	dioxane	**L1**	33
2	NiCl$_2$·glyme	dioxane	**L1**	34
3	NiBr$_2$·glyme	dioxane	**L1**	47
4	Ni(acac)$_2$	dioxane	**L1**	0
5	NiBr$_2$·glyme	THF	**L1**	44
6	NiBr$_2$·glyme	DME	**L1**	36
7	NiBr$_2$·glyme	dioxane	**L2**	57
8	NiBr$_2$·glyme	dioxane	**L3**	25
9	NiBr$_2$·glyme	dioxane	**L4**	16
10	NiBr$_2$·glyme	dioxane	**L5**	60
11	NiBr$_2$·glyme	dioxane	**L6**	60
12	NiBr$_2$·glyme	dioxane	**L7**	49
13[c]	NiBr$_2$·glyme	dioxane	**L5**	70
14[d]	-	dioxane	**L5**	0
15[e]	NiBr$_2$·glyme	dioxane	**L5**	0
16[f]	NiBr$_2$·glyme	dioxane	**L5**	0



[a]Reaction conditions: **1a** (0.10 mmol), **2a** (0.15 mmol), Ir(dFCF$_3$ppy)$_2$(dtbbpy)PF$_6$ (3 mol %), nickel salt (10 mol %) and ligand (20 mol %) in solvent (2 mL) at room temperature under the irradiation of 24 W CFL for 24 h. [b]Isolated yield. [c]Using 4 mL dioxane. [d]Without nickel salt. [e]Without photocatalyst. [f]Without visible light irradiation.

meta- or *ortho*-position of the benzene ring all reacted smoothly with **2a** to give **3ia**−**3ka** in 51−71% yield. Notably, multi-substituted aziridines **1l** and **1m** also proved to be suitable for the cross-coupling reaction with products **3la** and **3ma** being isolated in 30 and 60% yields, respectively. The naphthyl-substituted aziridine **1n** also worked well in the reaction, though giving product **3na** in only moderate yield. Interestingly, evaluation of a series of protecing groups (e.g., Ns, Ac) on the nitrogen atom of aziridines (e.g., **1o**, **1p**) showed that only the tosyl group was effective for the reaction. However, In contrast to Dolye's Ni-catalyzed Negishi cross-coupling of alkyl aziridines and organo zinc reagents,[5i] our current catalytic system could not accommodate alkyl aziridines. The use of multisubstituted aziridines such as **1q** and **1r**, for instance, did not produce any desired products. Further optimization studies, such as new photocatalyst design and ligand modification to address this limitation are ongoing.

Then, we continued to study the generality of this protocol by reacting a range of potassium alkyltrifluoroborates **2a**−**2h** with **1a** under standard conditions (Scheme 3). In addition to electronically neutral **2a**, it was found that substrates **2b**−**2d** bearing a weak electron-donating group (e.g., Me, Ph, ^{t}Bu) on the *para*-position of the benzene ring participated in the cross-coupling reaction very well to give the desired products **3ab**−**3ad** in moderate to good yields. Moreover, the reaction with halide

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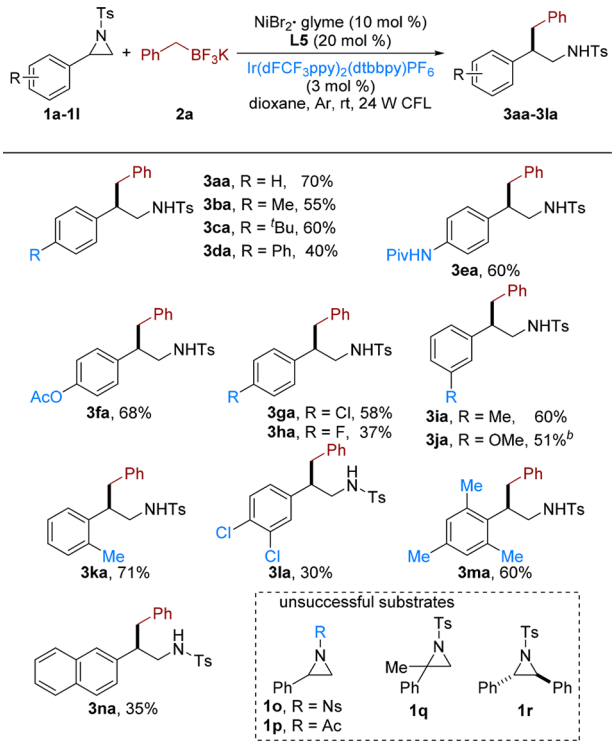
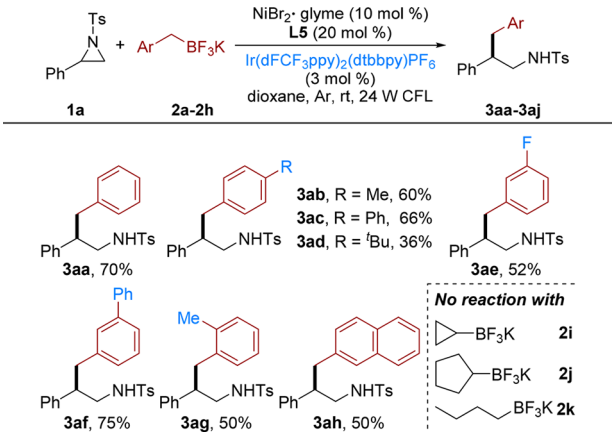
Scheme 2. Scope of Aziridines[a,b]



[a]**1a** (0.20 mmol), **2a** (0.3 mmol), $Ir(dFCF_3ppy)_2(dtbbpy)PF_6$ (3 mol %), $NiBr_2$·glyme (10 mol %), and **L5** (20 mol %) in dioxane (8 mL) at room temperature under irradiation of 24 W CFL for 48 h. [b]Isolated yield. [c]Ligand **L6** was used.

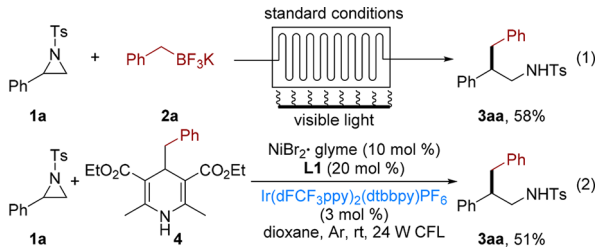
Scheme 3. Scope of Potassium Alkyltrifluoroborates[a,b]



[a]**1a** (0.20 mmol), **2a** (0.3 mmol), $Ir(dFCF_3ppy)_2(dtbbpy)PF_6$ (3 mol %), $NiBr_2$·glyme (10 mol %), and **L5** (20 mol %) in dioxane (8 mL) at room temperature under irradiation of 24 W CFL for 48 h. [b]Isolated yield.

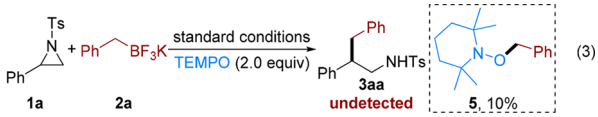
(e.g., F) and phenyl groups at the *meta*-position or a methyl group at the *ortho*-position also proceeded smoothly to give sulfonamides **3ae**−**3ag** in 50−75% yields. Potassium 2-naphthylmethyltrifluoroborate **1h** also reacted well to provide **3ah** in good yield. However, simple alkyltrifluoroborates such as **2i**−**2k** did not react under the standard conditions.

To further demonstrate the synthetic potential of this protocol, we applied a continuous flow process to the model reaction of **1a** and **2a** under standard conditions (eq 1, top). To



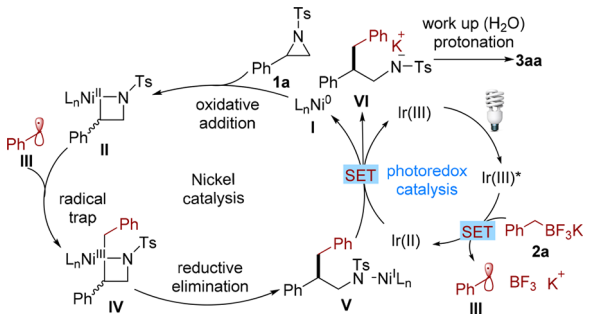
our delight, the reaction efficiency could be significantly improved to afford product **3aa** in 58% yield within 4 h. This finding also implies that the photoreaction process might be the rate-determining step. Notably, when using dimethyl fumarate **L1** as a ligand, 4-benzyl-1,4-dihydropyridine **4** can also serve as a benzyl radical precursor to react with aziridine **1a**, affording **3aa** in 51% yield (eq 2, bottom). This result opened a new way for further exploration of 1,4-dihydropyridines in the sp^3-sp^3 cross-coupling reaction.[14]

To gain some insight into the mechanism, we then performed a series of control experiments with substrates **1a** and **2a**. Upon addition of 2.0 equiv of radical trapping agent TEMPO, the model reaction was completely inhibited; and the benzyl radical was trapped by TEMPO to form compound **5** in 10% yield (eq 3). Surprisingly, all of the attempts to use of enantiopure 2-phenyl-1-tosylaziridine **1a** met failure, resulting in a complete loss of stereochemical information.[5a,13]



Then, we postulated a plausible mechanism for the present dual photoredox and nickel-catalyzed cross-coupling reaction (Scheme 4). First, the active Ni(0) catalyst **I**, formed in situ from

Scheme 4. Proposed Mechanism



the Ni(II) precatalyst, undergoes an oxidative insertion into the more hindered C−N bond of aziridine **1a** to afford the azanickelacyclobutane **II**. The complete regioselectivity can be attributed to the distinct electronic property of the electron-defficient olefin ligand. Meanwhile, **2a** was converted to benzylic radical **III** by the photoexcited state Ir(III)* through a SET oxidation process. Then, the Ni(II) species **II** would rapidly capture the resultant benzylic radical **III** to give alkylnickel(III) intermediate **IV**. Reductive elimination of intermediate **IV** gives Ni(I) species **V**, which undergoes another SET reduction by the reduced form of the photocatalyst Ir(II) to furnish product **3aa** via intermediate **VI** upon protonation, with release of ground sate photocatalyst Ir(III), closing both catalytic cycles.

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In conclusion, we have developed the first example of dual photoredox and nickel-catalyzed cross-coupling of aziridines and potassium alkyltrifluoroborates. The protocol features broad substrate scope, high functional group tolerance, exclusive regioselectivity, and mild redox-neutral conditions, providing complementary access to β-substitued amines.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.7b03747.

Experimental procedures, full analysis data for new compounds, and copies of NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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