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Access to Functionalized Isoquinoline *N*-Oxides *via* Sequential Electrophilic Cyclization/Cross-Coupling Reactions

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Abstract: Electrophilic cyclization of 2-alkynylbenzaldoximes with various electrophiles leads to the formation of 4-iodoisoquinoline *N*-oxides or 4-bromoisoquinoline *N*-oxides under mild conditions. The reaction can be transferred to highly functionalized isoquinoline *N*-oxides *via* palladium-catalyzed cross-coupling reactions.

Keywords: 2-alkynylbenzaldoximes; cross-coupling reaction; electrophilic cyclization; isoquinoline *N*-oxides

Introduction

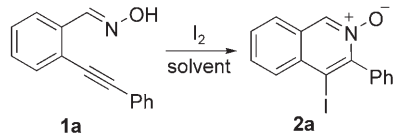
The increasing significance of combinatorial chemistry in pharmaceutical and material sciences demands the development of new strategies to synthesize a collection of analogues of interesting compounds.[1] As a privileged fragment, the isoquinoline core is a ubiquitous subunit in many alkaloids with remarkable biological activities.[2] Among these, isoquinoline *N*-oxide is an important class of isoquinoline derivatives. Moreover, they are also valuable Lewis basic organocatalysis in organic synthesis.[3] In addition, applications of these molecules have been discovered in materials science due to their interesting optochemical/physical properties, such as charge-transfer and metal (Li^+/Mg^{2+}) sensor effects and use as a radical initiator for atom-transfer radical polymerizations.[4] The importance of isoquinoline *N*-oxides has stimulated the development of a number of approaches for the synthesis of the isoquinoline *N*-oxide ring system.[5,6] However, most of them are still conducted by oxidation of parent nitrogen heterocycles and the diversity could not be easily introduced in the scaffold. Thus, it is highly desired to develop efficient and general synthetic methods for access to functionalized isoquinoline *N*-oxides in order to build up these molecules in a combinatorial format.

The electrophilic annulation of alkynes has proven to be extremely effective for the synthesis of a wide variety of carbocycles and heterocycles.[7] Recently, we found that *o*-alkynylbenzaldehyde was a versatile building block in multicomponent reactions for construction of the 1,2-dihydroisoquinoline skeleton.[8] In the reaction process, a 2-(1-alkynyl)arylaldimine[9,10] was believed to be the key intermediate for further transformation. Prompted by these results, we envisioned that 2-alkynylbenzaldoximes could be also utilized as starting material for synthesis of N-heterocycles due to the structural similarity with 2-(1-alkynyl)arylaldimines. Herein, we report a highly efficient and general method for the generation of functionalized isoquinoline *N*-oxides *via* sequential electrophilic cyclization/cross-coupling reactions of 2-alkynylbenzaldoximes under mild conditions.

Results and Discussion

As mentioned above, the electrophilic cyclization of heteroatomic nucleophiles such as oxygen, nitrogen, sulfur, and phosphorus species with tethered alkynes has proven to be an effective method for preparing a large variety of heterocyclic ring systems.[11] The electrophiles such as iodine, bromine, ICl, and NBS were commonly used in the reaction since the resulting iodo- or bromo-containing products are readily elaborated to more complex products by using known organopalladium chemistry. In preliminary studies, we in-

vestigated the electrophilic cyclization between the 2-alkynylbenzaldehyde oxime **1a** and iodine and found that the reaction took place in the presence of dichloromethane as solvent at room temperature (Scheme 1). This reaction was highly effective and the



CH_2Cl_2, 92% yield; Et_2O, 82% yield; toluene, 80% yield; $(CH_2Cl)_2$, 79% yield; THF, 56% yield; MeCN, 66% yield.

Scheme 1. Electrophilic cyclization of 2-alkynylbenzaldoxime **1a** with iodine in different solvents.

desired product **2a** was generated in 92% yield after 24 h. The structure of **2a** was verified by ^1H and ^{13}C NMR, mass spectroscopy, as well as X-ray diffraction analysis (Figure 1, for details, see Supporting Information). Other solvents were also screened, which revealed that dichloromethane was the best choice.

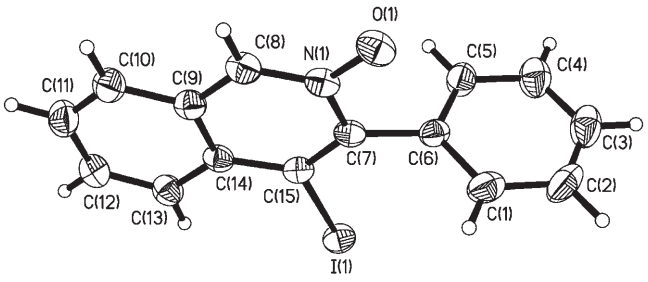
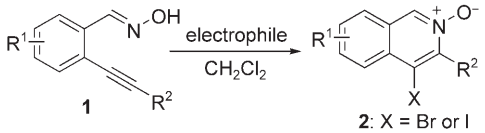


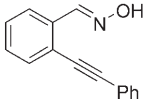
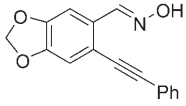
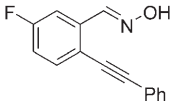
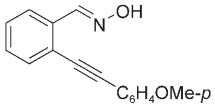
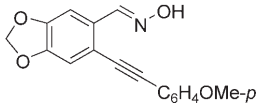
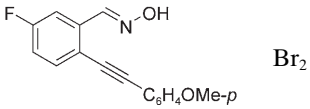
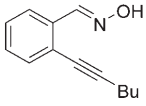
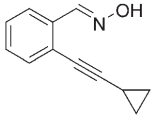
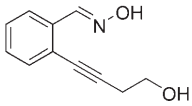
Figure 1. ORTEP diagram of 4-iodoisoquinoline *N*-oxide **2a**.

With this result in hand, the scope of this reaction was then investigated, and the results are summarized in Table 1. From Table 1, we found that the conditions have proven to be useful for a range of 2-alkynylbenzaldehyde oxime **1** and electrophiles. For instance, reaction of 2-alkynylbenzaldehyde oxime **1a** and ICl was finished in 10 min and the expected product **2a** was obtained in 93% yield (Table 1, entry 2). An almost quantitative yield of product **2b** was obtained when bromine was utilized as reactant (Table 1, entry 4: 99% yield). A slightly lower yield was observed when NBS was used as replacement (Table 1, entry 5: 75% yield). Other 2-alkynylbenzaldehyde oximes were also employed in the reaction of iodine or bromine. 2-Alkynylbenzaldehyde oxime **1b** reacted with iodine leading to the formation of isoquinoline-*N*-oxide **2c** in 88% yield (Table 1, entry 6), while a 25% yield of product **2d** was generated when iodine was replaced by bromine (Table 1, entry 7). This may presumably be due to the high reactivity of substrate

Table 1. Electrophilic cyclization of 2-alkynylbenzaldoxime with various electrophiles.



electrophile: I_2, ICl, NIS, Br_2, NBS

Entry	Alkynylbenzaldehyde oxime **1**	Electrophile	Product **2** (X)	Yield [%][a]
1		I_2	**2a** (I)	92
2		ICl	**2a** (I)	93
3	**1a** 	NIS	**2a** (I)	32
4		Br_2	**2b** (Br)	99
5		NBS	**2b** (Br)	75
6		I_2	**2c** (I)	88
7	**1b** 	Br_2	**2d** (Br)	25
8		I_2	**2e** (I)	92
9	**1c** 	Br_2	**2f** (Br)	99
10		I_2	**2g** (I)	91
11	**1d** 	Br_2	**2h** (Br)	99
12		I_2	**2i** (I)	89
13	**1e** 	Br_2	**2j** (Br)	94
14	**1f** 	Br_2	**2k** (Br)	90
15	**1g** 	Br_2	**2l** (Br)	85
16		I_2	**2m** (I)	90
17	**1h** 	Br_2	**2n** (Br)	94
18	**1i** 	Br_2	**2o** (Br)	64

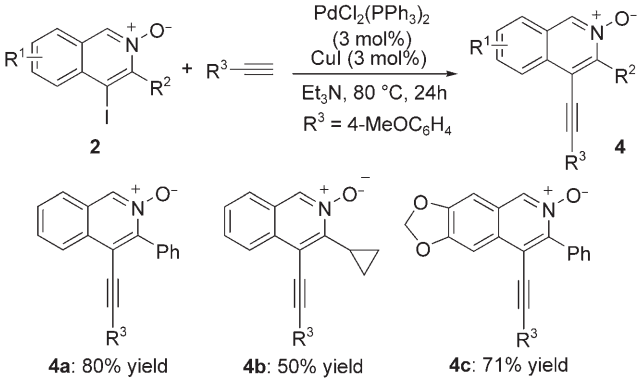
[a] Isolated yield based on 2-alkynylbenzaldoxime **1**.

1b in the reaction of bromine since many by-products were observed during the reaction process. The yield could be increased to 45% when the reaction was performed at −10 °C (data not shown in Table 1). Reaction of fluoro-substituted 2-alkynylbenzaldehyde oxime **1c** with iodine or bromine gave rise to the corresponding product **2e** or **2f** in 92% and 99% yields, respectively (Table 1, entries 8 and 9). When phenyl group attached on the triple bond was changed to a 4-methoxyphenyl group, the reactions also proceeded

smoothly to furnish the desired product in excellent yields (Table 1, entries 10–14). 2-Alkynylbenzaldehyde oximes **1g** and **1h** were also examined and similar results were observed for reactions of iodine or bromine (Table 1, entries 15–17). Interestingly, it was found that a hydroxy group as substituent in the substrate **1i** was well tolerated under these conditions and the 4-bromoisoquinoline *N*-oxide **2o** could be isolated in 64% yield (Table 1, entry 18).

After the successful generation of 4-bromo- or 4-iodoisoquinoline *N*-oxide **2**, we considered to introduce more diversity into the isoquinoline *N*-oxide scaffold *via* palladium-catalyzed cross-coupling reactions. Thus, 4-bromoisoquinoline *N*-oxide **2b** or **2n** was reacted with sodium tetraphenylborate to give the desired 3,4-disubstituted isoquinoline *N*-oxide **3a** or **3b** in 93% or 83% yield, respectively [Scheme 2, Eq. (1)]. Similarly, the reaction of 4-bromoisoquinoline *N*-oxide **2b** with phenylboronic acid furnished the expected product **3a** in 99% yield [Scheme 2, Eq. (2)]. Isoquinoline *N*-oxide **2j** reacted smoothly with 4-methylphenylboronic acid leading to the corresponding product **3c** in 78% yield [Scheme 2 Eq. (3)]. Fluoro-substituted isoquinoline *N*-oxide **2f** was also a good partner in the cross-coupling reaction with 4-methylphenylboronic acid. As expected, the corresponding 3,4-disubstituted isoquinoline *N*-oxide **3d** was generated in 95% yield [Scheme 2, Eq. (4)].

The Sonogashira coupling reactions of 4-iodoisoquinoline *N*-oxide **2** with 4-methoxyphenylacetylene were also examined (Scheme 3). Under standard conditions, the coupling reactions proceeded well to generate the desired product **4** in moderate to good yield.



Scheme 3. Synthesis of 3,4-disubstituted isoquinoline *N*-oxides *via* palladium-catalyzed Sonogashira coupling.

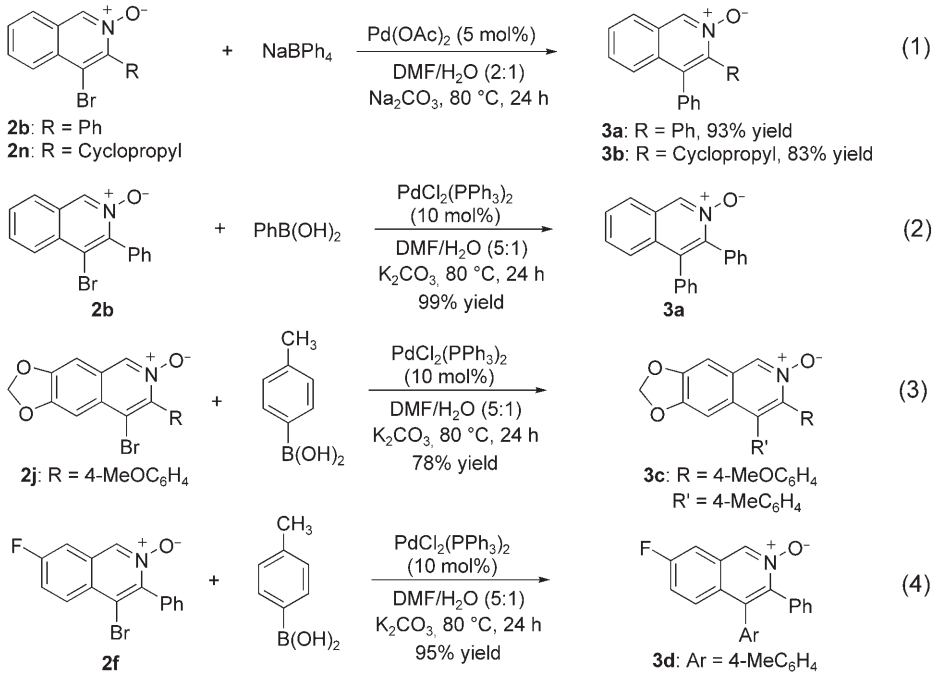
Conclusions

In summary, we have described a novel and efficient method for the synthesis of highly functionalized isoquinoline *N*-oxides *via* sequential electrophilc cyclization/cross-coupling reactions of 2-alkynylbenzaldoximes. Application of 2-alkynylbenzaldoximes in other transformations is currently under investigation, and the results will be reported in due course.

Experimental Section

General Procedure for Preparation of 2-Alkynylbenzaldoxime 1[12]

A solution of 2-alkynylbenzaldehyde (3.0 mmol), hydroxylamine hydrochloride (6 mmol, 2.0 equiv.), pyridine



Scheme 2. Synthesis of 3,4-disubstituted isoquinoline *N*-oxides *via* palladium-catalyzed Suzuki–Miyaura reactions.

(6.0 mmol, 2.0 equiv.) in C_2H_5OH (15 mL) was stirred under refluxed for 2 h. After completion of reaction as indicated by TLC, the solvent was evaporated and the reaction residue then quenched with water (10 mL), extracted with EtOAc (2×30 mL), dried by anhydrous Na_2SO_4. Evaporation of the solvent followed by purification on silica gel provided the corresponding 2-alkynylbenzaldoxime **1**.

General Procedure for Electrophilic Cyclization of 2-Alkynylbenzldoxime 1 with Various Electrophiles

The electrophile (1.2 equiv.) in 2 mL of CH_2Cl_2 was added dropwise to a solution of 2-alkynylbenzaldoxime (0.30 mmol) in 4 mL of CH_2Cl_2. The reaction mixture was stirred at room temperature for a period of time (10 min: Br_2, ICl, or NIS; 24 h: NBS and I_2). The reaction mixture was then diluted with CH_2Cl_2 (50 mL), washed with saturated aqueous $Na_2S_2O_3$ (25 mL), dried (Na_2SO_4) and filtered. The solvent was evaporated under reduced pressure and the product **2** was isolated by chromatography on a silica gel column.

Data of a selected example: 4-iodo-3-phenylisoquinoline N-oxide **2a**: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.38$ (d, $J = 6.8$ Hz, 2H), 7.48–7.58 (m, 3H), 7.59–7.69 (m, 3H), 8.06 (d, $J = 8.3$ Hz, 1H), 8.85 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 122.1$, 124.9, 127.3, 128.5, 128.9, 129.4, 129.7, 129.8, 129.9, 133.4, 136.0, 147.7; MS (ESI): $m/z = 348$ ($M^+ + H$); elemental analysis calcd. (%) for $C_{15}H_{10}INO$: C 51.90, H 2.90, N 4.03; found: C 51.64, H 2.88, N 3.98.

General Procedure for Synthesis of 3,4-Disubstituted Isoquinoline *N*-Oxide 3 *via* Palladium-Catalyzed Suzuki–Miyaura Reaction

A solution of 4-bromoisoquinoline *N*-oxide **2** (0.30 mmol), sodium tetraphenylborate (0.15 mmol, 0.5 equiv.) or arylboronic acid (0.45 mmol, 1.5 equiv.), palladium catalyst (5 mol%), base (1.2 mmol, 4.0 equiv.) in DMF/H_2O (2.0 mL) was stirred at 80 °C under N_2 for 24 h. After completion of reaction as indicated by TLC, the solvent was evaporated and the residue quenched with water (10 mL), extracted with EtOAc (2×10 mL), and dried by anhydrous Na_2SO_4. Evaporation of the solvent followed by purification on silica gel provided the corresponding 3,4-disubstituted isoquinoline *N*-oxide **3**.

Data of a selected example: 3,4-diphenylisoquinoline N-oxide **3a**: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.07$–7.10 (m, 2H), 7.19–7.28 (m, 5H), 7.34–7.46 (m, 3H), 7.50 (dt, $J = 1.5$, 6.8 Hz, 1H), 7.60 (t, $J = 6.8$ Hz, 1H), 7.77 (d, $J = 8.3$ Hz, 1H), 7.96 (t, $J = 6.8$ Hz, 1H), 9.08 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 124.9$, 126.2, 127.7, 127.8, 128.0, 128.3, 128.6, 129.0, 129.1, 129.7, 130.3, 130.7, 131.9, 134.7, 136.5, 137.0, 146.0; MS (ESI): $m/z = 298$ ($M^+ + H$); HR-MS: $m/z = 298.1221$, calcd. for $C_{21}H_{16}NO$ ($M^+ + H$): 298.1232.

General Procedure for Synthesis of 3,4-Disubstituted Isoquinoline *N*-Oxides 4 *via* Palladium-Catalyzed Sonogashira Reaction

A solution of 4-iodoisoquinoline *N*-oxide **2** (0.30 mmol), 4-methoxyphenylacetylene (0.45 mmol, 1.5 equiv.), $PdCl_2(PPh_3)_2$ (3 mol%), CuI (3 mol%) in Et_3N (2.0 mL) was stirred at 80 °C under N_2 for 24 h. After completion of reaction as indicated by TLC, the solvent was evaporated and the residue quenched with water (10 mL), extracted with EtOAc (2×10 mL), dried by anhydrous Na_2SO_4. Evaporation of the solvent followed by purification on silica gel provided the corresponding 3,4-disubstituted isoquinoline *N*-oxide **4**.

Data of a selected example: 4-[2-(4-ethoxyphenyl)ethynyl]-3-phenylisoquinoline N-oxide **4a**: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 3.81$ (s, 3H), 6.83 (d, $J = 8.8$ Hz, 2H), 7.22 (d, $J = 8.8$ Hz, 2H), 7.48–7.57 (m, 3H), 7.61–7.75 (m, 5H), 8.30 (d, $J = 8.8$ Hz, 1H), 8.87 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 55.3$, 82.2, 101.4, 114.1, 120.0, 124.7, 125.9, 127.9, 128.5, 129.2, 129.3, 129.4, 130.6, 132.2, 133.2, 136.3, 148.9, 160.4; MS (ESI): $m/z = 352$ ($M^+ + H$); HR-MS: $m/z = 352.1339$, calcd. for $C_{24}H_{18}NO_2$ ($M^+ + H$): 352.1338. (For details, please see Supporting Information.)

CCDC 690391 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information

Experimental procedures, characterization data, as well as copies of ^{1}H and ^{13}C NMR of all compounds are available as Supporting Information.

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