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# Rh(III)-catalyzed atroposelective C–H alkynylation of 1-aryl isoquinolines with hypervalent iodine–alkyne reagents†

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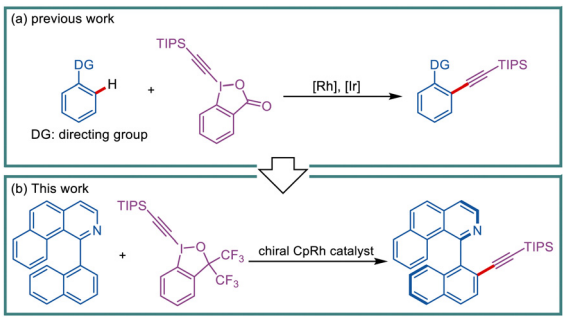
**An efficient Rh(III)-catalyzed enantioselective C–H alkynylation of isoquinolines is disclosed. The C–H alkynylation of 1-aryl isoquinolines with hypervalent iodine–alkyne reagents proceeded in DMA at room temperature in the presence of 2.5 mol% chiral SCpRh(III) complex along with 20 mol% $AgSbF_6$, providing axially chiral alkynylated 1-aryl isoquinolines in excellent yields (up to 93%) and enantioselectivity (up to 95% ee). The diverse transformations of the product further enhance the potential utility of this reaction.**

Hypervalent iodine reagents (HIRs) have been established as versatile and useful reagents for synthetic organic transformations due to their exceptional reactivity.[1] Among them, ethynylbenziodoxolone (EBX) reagent is one of the most widely used hypervalent iodine reagents for the direct alkynylation of heteroatom or carbon nucleophiles.[2] In particular, great achievements have been made in transition-metal-catalyzed C–H alkynylation reactions by taking advantage of EBX reagents as the coupling partners (Scheme 1a).[3] In 2009, pioneering works on gold or palladium-catalyzed C–H alkynylation of electron-rich aromatic substrates including indoles, pyrroles and anilines with hypervalent alkynyl iodine reagents were developed by Waser and co-workers.[3d] Later on, Loh and coworkers reported an elegant example of rhodium-catalyzed electronically reversed Sonogashira coupling of electron-poor arenes, affording the alkynyl benzamide products in up to 99% yield.[3e] Shortly afterwards, Li and coworkers developed efficient Rh(III)- and Ir(III)-catalyzed *ortho* C–H alkynylation reactions of diversified arenes using hypervalent iodine–alkyne reagents.[3j] Both electron-poor and electron-rich arenes bearing different directing groups are viable substrates in this transformation. Although much progress has been accomplished, it remains challenging to develop Rh(III)-catalyzed enantioselective C–H alkynylation by employing EBX reagents.

The synthesis of axially chiral biaryls has been extensively investigated since they broadly exist in natural products, pharmaceuticals, biologically active molecules, chiral ligands, and organocatalysts.[4] Among these methods, the atroposelective C–H functionalization of achiral biaryls represents one of the most efficient and straightforward approaches to access axially chiral biaryls.[5] In this regard, the synthesis of axially chiral alkyne-functionalized biaryls has been widely explored *via* transition-metal-catalyzed atroposelective C–H alkynylation.[6] In 2018, Shi and coworkers demonstrated a highly practical and efficient strategy for the construction of a broad range of enantiomerically enriched axially chiral biaryls in excellent yields (up to 99%) and enantioselectivity (up to >99% ee) through Pd-catalyzed atroposelective C–H alkynylation.[7] Later on, they found that the atropisomers containing one or even two five-membered rings connected through C–C or C–N bonds were compatible with the same strategy.[8] While these elegant achievements exhibited the feasibility of catalytic asymmetric synthesis of alkynyl-containing atropisomers, the application of EBX reagents in transition-metal-catalyzed atroposelective C–H




Scheme 1 Transition-metal-catalyzed C–H alkynylation reactions with EBX reagents.

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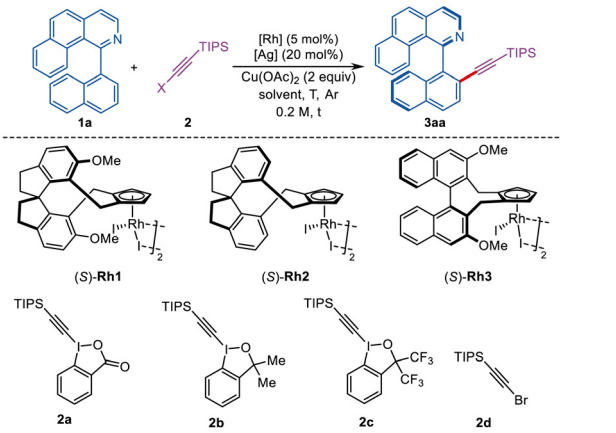
Table 1 Optimization of the reaction conditions[a]




| Entry | [Rh] | 2 | Solvent | $T$ (°C) | $t$ (h) | Yield[b] (%) | ee[c] (%) |
|---|---|---|---|---|---|---|---|
| 1 | (*S*)-**Rh1** | **2a** | $^t$AmylOH | 80 | 12 | 97 | 59 |
| 2 | (*S*)-**Rh2** | **2a** | $^t$AmylOH | 80 | 12 | 91 | 33 |
| 3 | (*S*)-**Rh3** | **2a** | $^t$AmylOH | 80 | 12 | 40 | −13 |
| 4 | (*S*)-**Rh1** | **2a** | DMA | 80 | 12 | 86 | 72 |
| 5 | (*S*)-**Rh1** | **2b** | DMA | 80 | 24 | 30 | 12 |
| 6 | (*S*)-**Rh1** | **2c** | DMA | rt | 24 | 88 | 84 |
| 7 | (*S*)-**Rh1** | **2d** | DMA | rt | 24 | 63 | 80 |
| 8[d] | (*S*)-**Rh1** | **2c** | DMA | rt | 24 | 82 | 87 |
| 9[d] | (*S*)-**Rh1** | **2c** | DMA | rt | 48 | 88 | 87 |
| 10[de] | (*S*)-**Rh1** | **2c** | DMA | rt | 48 | 52 | 90 |

[a] Reaction conditions: **1a** (0.05 mmol), **2** (0.1 mmol), [Rh] (5 mol%), $AgSbF_6$ (20 mol%), $Cu(OAc)_2$ (0.1 mmol) in solvent (0.25 mL). [b] Isolated yield. [c] Determined by HPLC analysis with a chiral stationary phase. [d] No $Cu(OAc)_2$. [e] Under air.

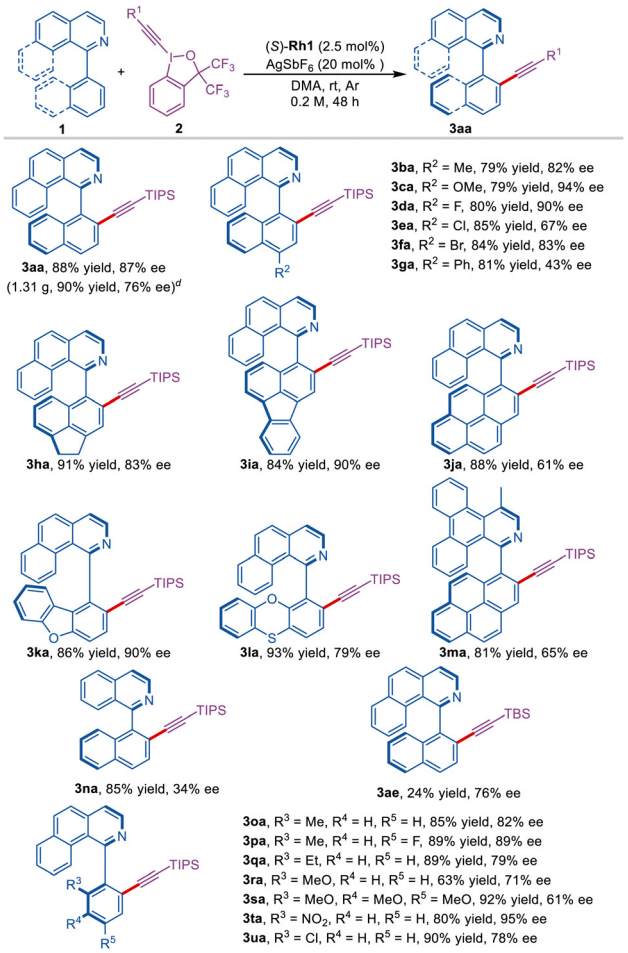
alkynylation remains undeveloped. With our continuous interest in Rh-catalyzed asymmetric C–H functionalization and synthesis of biaryl atropisomers,[9] we envisioned that Rh-enabled enantioselective C–H alkynylation of 1-aryl isoquinoline with EBX might efficiently furnish *enantio*-enriched alkynyl biaryls. Herein, we report the highly atroposelective synthesis of 1-aryl isoquinolines *via* CpRh-catalyzed C–H alkynylation reaction. This strategy provides efficient access to a wide range of axially chiral alkynylated isoquinolines.

We commenced our studies with the reaction of 1-(naphthalen-1-yl)benzo[*h*]isoquinoline **1a** with 1-[(triisopropylsilyl) ethynyl]-1,2-benziodoxol-3(1*H*)-one (TIPS-EBX) **2a** at 80 °C in the presence of 5 mol% of (*S*)-**Rh1**,[9d] 20 mol% of $AgSbF_6$, and 2 equivalents of $Cu(OAc)_2$ in $^t$AmylOH. Gratifyingly, the desired axially chiral alkynylated isoquinoline **3aa** was obtained in 97% yield and 59% ee (Table 1, entry 1). **3aa** was proved to be conformationally stable, and no erosion of its ee value was observed after heating at 170 °C for 10 h. Encouraged by these preliminary results, various chiral CpRh catalysts were screened, and (*S*)-**Rh1** was confirmed to be the optimal one (entries 2–3, for complete catalyst screening, see Table S1, ESI†). The solvent effect revealed that DMA was the optimal choice, giving rise to **3aa** in 86% yield and 72% ee (see Table S2 for details, ESI†). The utilization of other silver salts including $AgNTf_2$, AgOTf and $AgPF_6$ *etc.* has no obvious influence on the enantioselectivity (see Table S3 for details, ESI†). In addition, other reaction parameters such as copper salts, concentration, and additives were investigated, and the results in terms of yield and enantioselectivity were not further improved (see Tables S4–S6 for details, ESI†). Notably, when the reaction was performed at room temperature, the enantioselectivity was increased to 78% ee. Further lowering the reaction temperature to 0 °C resulted in a dramatically decreased yield (51%, 88% ee) (see Table S7 for details, ESI†). Subsequently, the TIPS-protected alkynylation reagents **2b–2d** were screened (entries 5–7, see Table S8 for other alkynylation reagents, ESI†). The use of EBX reagent **2c**[10] bearing *gem*-ditrifluoromethyl groups gave the best results in terms of yield and enantioselectivity (entry 6, 88% yield, 84% ee). It is noteworthy that TIPS-protected alkynyl bromide (**2d**) was also compatible in this reaction with slightly decreased yield and enantioselectivity (entry 7, 63% yield, 80% ee). The ee value of **3aa** could be further improved when this C–H alkynylation reaction with **2c** was carried out in the absence of $Cu(OAc)_2$. (Entry 8, 82% yield, 87% ee. See Table S10 for details, ESI†) Prolonging the reaction time to 48 h gave the optimal reaction conditions, affording **3aa** in 88% yield and 87% ee (entry 9). It is noteworthy that this reaction could be accomplished under an air atmosphere, leading to the alkynylated product in 52% yield and 90% ee (entry 10). Overall, the optimal reaction conditions were identified as the following: **1a** (1 equiv.), **2c** (2 equiv.), (*S*)-**Rh1** (2.5 mol%), $AgSbF_6$ (20 mol%) under argon in DMA at room temperature for 48 h.

With the optimal reaction conditions in hand, the atroposelective C–H alkynylation of substituted 1-aryl isoquinolines **1** with **2c** was first investigated (Scheme 2). The isoquinolines bearing either a 4-methyl or 4-methoxy group on the naphthalene ring gave the desired products **3ba–3ca** in 79% yield and good enantioselective control (82–94% ee). The substrates bearing F, Cl, Br and a phenyl group on the 4-position of the naphthalene ring were also well compatible, affording **3da–3ga** with good yields and moderate to excellent enantioselectivity (80–85% yields, 43–90% ee). It is noteworthy that the polycyclic naphthalene substrates were also tolerated, furnishing products in good to excellent yields and moderate to excellent enantioselectivity (**3ha–3ja**, 84–91% yields, 61–90% ee). The benzoisoquinoline substrates containing heteroaromatic rings were compatible with this reaction, giving **3ka** in 86% yield with 90% ee and **3la** in 93% yield with 79% ee, respectively. Employing the π-extended benzoisoquinoline **1m** as a substrate led to the alkynylated atropisomer **3ma** in 81% yield with 65% ee. In addition, the isoquinoline substrate **1n** furnished **3na** with poor enantioselectivity, likely due to the less steric effect (**3n**, 85% yield, 34% ee). Notably, a gram-scale reaction of **1a** with **2c** was conducted under the standard conditions, providing **3aa** in 90% yield (1.31 g) with 76% ee.

Next, the benzoisoquinolines bearing *ortho*-substituted phenyl groups were explored (Scheme 2). When substrates bearing 2-methyl or 2-ethyl groups on the benzene ring were applied in this reaction, **3oa–3qa** were obtained smoothly with moderate to excellent enantioselectivity (85–89% yields, 79–89% ee). The *ortho*-methoxy-substituted substrates **1r–1s** gave the desired products **3ra–3sa** in 63–92% yields and 61–71% ee.

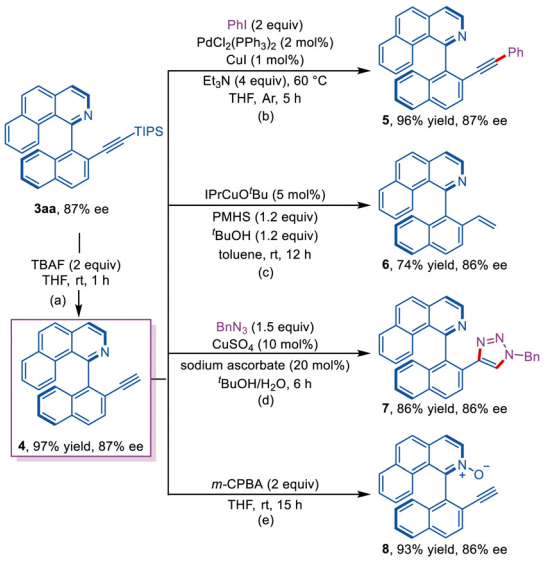
 




Scheme 2 Rh-catalyzed C–H alkynylation reactions with EBX reagents. [a] Reaction conditions: **1** (0.2 mmol), **2** (0.4 mmol), (*S*)-**Rh1** (2.5 mol%), and $AgSbF_6$ (20 mol%) in DMA (1 mL). [b] Isolated yield. [c] The ee values were determined by HPLC analysis on a chiral stationary phase. [d] Reaction conditions: **1** (3 mmol), **2** (6 mmol), (*S*)-**Rh1** (2.5 mol%), and $AgSbF_6$ (20 mol%) in DMA (15 mL).

Interestingly, the *ortho* $NO_2$-substituted substrate gave the best ee value, and this is probably due to the nitro group being coordinated with rhodium (**3ta**, 80% yield, 95% ee). It should be noted that the *ortho* Cl-substituted substrate was also compatible with this reaction (**3ua**, 90% yield, 78% ee). In addition, the protecting group TIPS of **2c** replaced by TBS (*t*-butyldimethylsilyl) resulted in a dramatically decreased yield (**3ae**, 24% yield, 76% ee).

To demonstrate the potential utility of **3aa**, the synthetic applications of the alkynylation product were investigated. By treatment of **3aa** with TBAF in THF at room temperature, the TIPS group could be readily removed to afford the terminal alkyne **4** in 97% yield with 87% ee (Scheme 3a). Then, **4** was utilized as a key intermediate for the synthesis of various axially chiral 1-aryl isoquinolines. The Sonogashira coupling reaction of **4** was carried out to afford the phenylacetylene substituted product **5** in 96% yield. The absolute configuration of **5** was assigned as $R_a$ according to the reported literature (Scheme 3b).[9i] The configurations of other products were assigned by analogy.

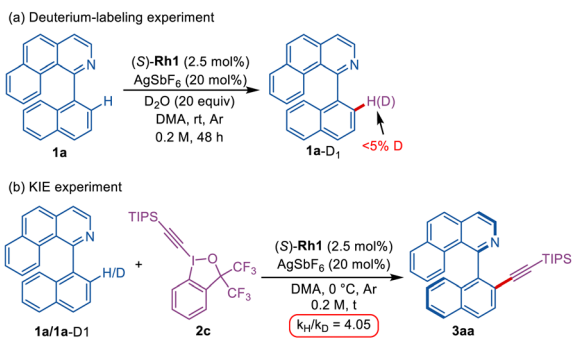



Scheme 3 Representative derivatizations.

Highly selective semi-hydrogenation of alkyne was achieved in 74% yield (Scheme 3c).[11] Moreover, the Cu(I)-catalyzed click reaction of **4** with benzyl azide was performed under mild conditions to give triazole product **7** in 86% yield and 86% ee (Scheme 3d).[12] Finally, the *N*-oxidation reaction of **4** treated with *m*-CPBA furnished *N*-oxide **8** in 93% yield without loss of enantioselectivity (Scheme 3e).

To shed light on the mechanism of this C–H alkynylation reaction, H/D exchange of **1a** was performed in the presence of $D_2O$ under standard conditions. No deuterium incorporation indicated that the C–H cleavage is irreversible (Scheme 4a). The kinetic isotope effect was then measured from the alkynylation reaction of **1a**-$D_1$ and **1a**, and a large KIE value of 4.05 suggests that the C–H bond activation might be involved in the turnover-limiting step (Scheme 4b).[13]

Based on the above mechanistic studies and previous report,[14] a plausible mechanism for atroposelective C–H alkynylation is proposed (Fig. S3, ESI†). Following path a, the chiral CpRh complex firstly undergoes oxidative addition with **2c** to form the CpRh(v) complex **I**. Subsequently, the cyclometalation of **1a** with the active CpRh(v) complex **I** affords an intermediate **III**, along with the generation of alcohol **9**. Finally, the alkanylated




Scheme 4 Mechanistic studies.

product **3aa** is released after the reductive elimination of rhodacycle **III** and regenerates the Rh(III) catalyst. Another pathway involving the C–H activation of 1-aryl benzoisoquinoline first, followed by oxidative addition with **2c** cannot be completely excluded at present.

In summary, we have developed highly atroposelective synthesis of alkynylated 1-aryl isoquinolines based on Rh(III)-catalyzed C–H alkynylation of 1-aryl isoquinolines with hypervalent iodine–alkyne reagents. A broad scope of substrates has been defined, and the C–H Sonogashira coupling reaction proceeded in excellent yields and enantioselectivity under mild reaction conditions. It is noteworthy that diverse transformations were realized for the synthesis of structurally diverse 1-aryl isoquinolines with potential applications. Further development of transition-metal-catalyzed enantioselective C–H functionalization reactions for the construction of axially chiral biaryls is underway in our laboratory.

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## Conflicts of interest

The authors declare no competing financial interest.

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