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Enantioselective synthesis of 3-aryl-phthalides through a nickel-catalyzed stereoconvergent cross-coupling reaction†

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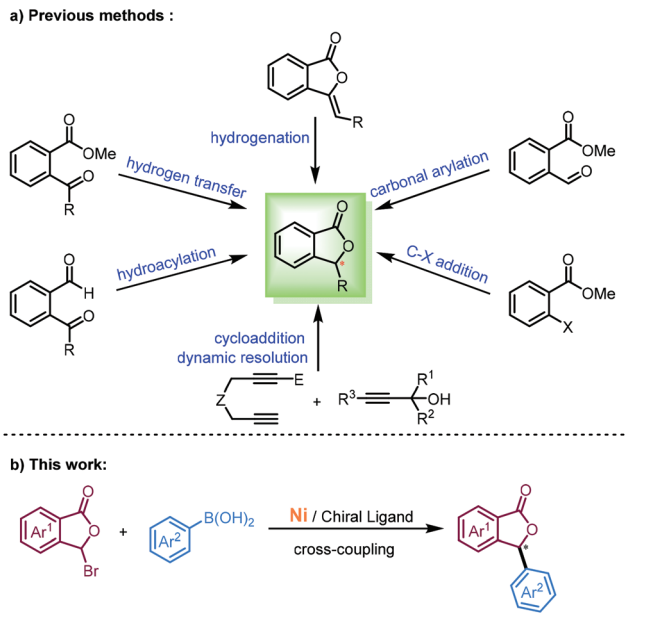
A nickel-catalyzed asymmetric Suzuki–Miyaura cross-coupling of racemic 3-bromo-phthalides and arylboronic acids was realized for the synthesis of diverse chiral 3-aryl-phthalides in moderate to excellent reaction yields. The reaction proceeded in a stereoconvergent manner and high enantioselectivities were observed for most examined examples. A number of functional groups like aldehyde, ester and bromide were well tolerated. Heteroaromatic boronic acids were also competent coupling partners in this reaction.

Phthalides, namely 3*H*-isobenzofuran-1-ones, are important structural motifs embedded in many natural products,[1] which often show a wide range of biological activities such as antioxidant,[2] antiplatelet,[3] antihyperglycemic,[4] and analgesic activities.[5] Among these, chiral 3-substituted phthalides are important members, and their enantioselective synthesis has received considerable research interest.[1,6] Although asymmetric reactions using chiral auxiliaries, reagents or precursors have proved to be applicable,[7] much effort has been devoted to the development of asymmetric transition metal-catalyzed processes such as hydrogenation/transfer hydrogenation,[8] dynamic resolution,[9] aldol/Michael reaction,[10] allylation/alkylation-lactonization,[11] addition-lactonization[12] sequential process, and cyclization reactions (Scheme 1).[13]

Transition metal-catalyzed cross-coupling reactions comprise efficient methods for the construction of C–C bonds.[14] Among them, the Suzuki–Miyaura reaction that utilizes organoboron reagents as coupling partners has been employed universally in both industry and academia.[15] Due to several serious problems like slow oxidative addition with alkyl electrophiles and the decomposition of alkyl organometallics *via* β-elimination, the traditional palladium-catalyzed Suzuki–Miyaura cross-coupling with alkyl (pseudo)halides was rather challenging.[16] In the meantime, nickel has received much attention as a superior catalyst for this kind of transformation. Furthermore, the nickel-catalyzed stereoconvergent coupling reaction of alkyl electrophiles could convert a racemic mixture of enantiomers to an enantioenriched product, representing a powerful method to construct chiral saturated hydrocarbon frameworks.[17–19] As the development of convenient preparation of diverse chiral 3-aryl-phthalides is still in demand,[6a]



Scheme 1 Transition metal-catalyzed synthesis of chiral 3-substituted phthalides.

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we envisioned that nickel-catalyzed asymmetric Suzuki–Miyaura cross-coupling may provide a flexible and modular strategy toward this goal.[20]

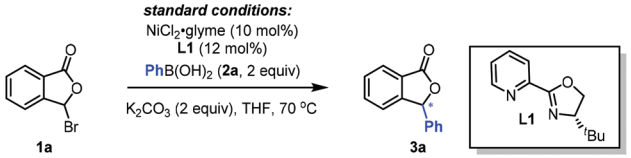
3-Halo-isobenzofuranones are widely used as electrophiles in the Friedel–Crafts reaction for the racemic synthesis of 3-aryl-phthalides.[21] We decided to use these as coupling partners for the nickel-catalyzed, stereoconvergent synthesis of chiral 3-substituted phthalides. Herein, we describe our success in achieving this goal (Scheme 1).

We started our investigation with 3-bromo-isobenzofuranone **1a** and phenylboronic acid **2a** as model substrates. Preliminary studies indicated that pyridyloxazoline ligand **L1** exhibited high activity and the reaction was accomplished in the presence of a nickel catalyst *in situ* generated by mixing 10 mol% $NiCl_2$·diglyme and 12 mol% **L1**. After extensive screening, the desired phthalide product **3a** was generated in an excellent yield with a very good ee value (Table 1, entry 1). A screening of bases showed that they had a crucial effect on the reaction. While the replacement of K_2CO_3 resulted in a lower reaction yield and enantioselectivity (Table 1, entry 2), the reaction was totally inhibited when Cs_2CO_3, K_3PO_4 or EtONa was used as the base (Table 1, entries 3–5), which was ascribed to a faster degradation of 3-bromo-isobenzofuranone with these bases. The reaction also proceeded smoothly in other ether solvents like dioxane, diglyme and dimethyl ether, but showed reduced efficiency (Table 1, entries 6–8). Attempts to further improve the enantioselectivity by performing the reaction at a lower temperature proved to be unsuccessful (Table 1, entry 9). Both reaction yield and enantioselectivity were decreased when a lower catalyst loading of 5 mol% was used (Table 1, entry 10).

On the basis of the previous literature, the bidentate N-ligands often played a crucial role in this kind of transformation. Thus, ligand screening was then performed to further improve the efficiency and enantioselectivity (Table 2). Although excellent reaction yields were also observed, the replacement of the *t*-Bu group of **L1** by less sterically hindered groups resulted in a significant loss in enantioselectivity. The introduction of CF_3 substitution at the 5- or 4-position of the pyridyl ring could slightly increase the enantioselectivities (**L5** and **L6**). While the steric hindrance around the nitrogen atom of the pyridyl ring was increased by switching the phenyl ring to the quinolinyl group, the reaction yield decreased significantly albeit with comparable enantioselectivity. The bis(oxazoline) ligands often are competent ligands in similar cross-couplings. However, all the tested bis(oxazoline) ligands were not effective at promoting the current transformation (**L8–L10**).[16]

To explore the scope of this nickel-catalyzed process, a variety of boronic acids with diverse steric and electronic properties were firstly examined in the reaction with 3-bromo-isobenzofuranone **1a** (Table 3). Under the optimized reaction conditions, a number of arylboronic acids with different substituents on the phenyl ring were coupled smoothly with 3-bromo-isobenzofuranone with moderate to very good levels of enantioselectivity. The reaction yield was affected by both the electronic and steric properties of the arylboronic acids. Compared with electron-withdrawing groups (**3d–3i**), electron-donating substituents had beneficial effects on the reaction yields (**3a–3c**). The sterically more hindered *ortho*-methyl substituted phenyl boronic acid gave a relatively lower yield (**3k**). Notably, several useful functional groups like halides (Cl and Br), ester and aldehyde were well tolerated, providing handles for further derivatizations (**3e**, **3f**, **3h** and **3i**). The replacement of the phenyl ring by the naphthyl group was compatible. A range of substrates containing heterocyclic fragments, such as

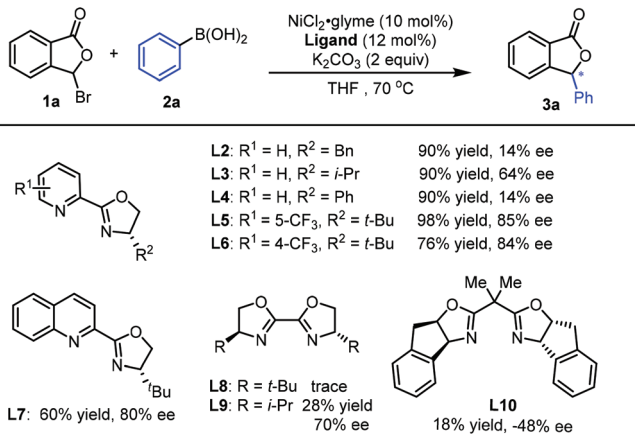
Table 1 Optimization of reaction parameters[a]



Entry	Deviation from standard conditions	Yield[b] (%)	ee[c] (%)
1	None	98	82
2	Na_2CO_3 instead of K_2CO_3	84	76
3	Cs_2CO_3 instead of K_2CO_3	Trace	—
4	K_3PO_4 instead of K_2CO_3	Trace	—
5	EtONa instead of K_2CO_3	Trace	—
6	Dioxane instead of THF	79	64
7	Diglyme instead of THF	90	70
8	Dimethyl ether instead of THF	74	78
9	50 °C instead of 70 °C	40	72
10	5 mol% $NiCl_2$·glyme and 6 mol% **L1**	50	67

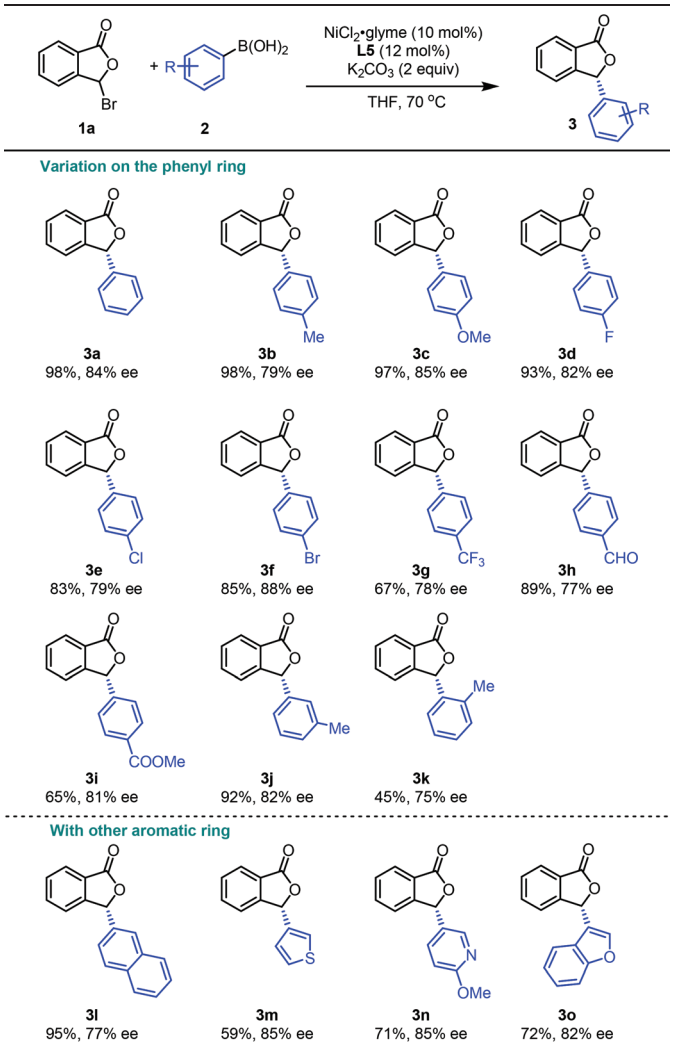
[a] Reactions were carried out at 70 °C for 12 h by using 3-bromo-isobenzofuranone **1a** (0.2 mmol), **2a** (0.4 mmol), Ni catalyst (0.02 mmol), **L1** (0.024 mmol), and K_2CO_3 (0.4 mmol) in THF (2.0 mL) unless otherwise noted. [b] Yield was determined by ^{1}H NMR using dibromomethane as the internal standard. [c] The ee value was determined by HPLC analysis on a chiral stationary phase.

Table 2 Ligand screening[a,b,c]



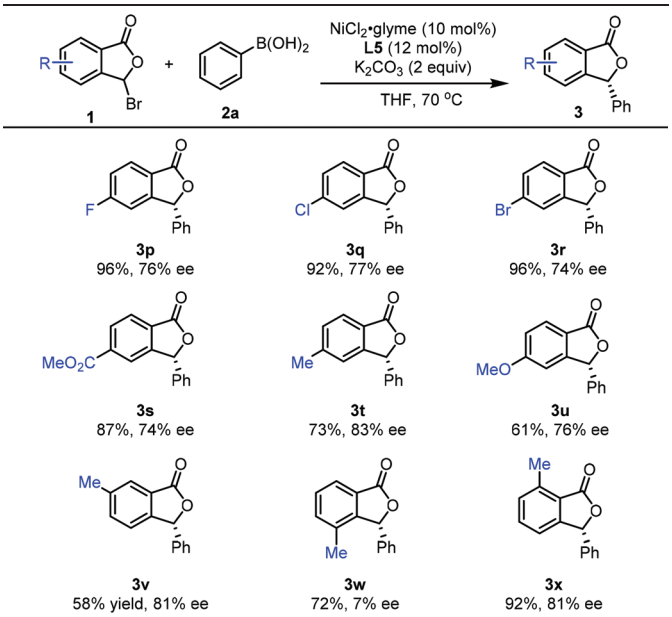
[a] Reactions were carried out at 70 °C for 12 h by using 3-bromo-isobenzofuranone **1a** (0.2 mmol), **2a** (0.4 mmol), Ni catalyst (0.02 mmol), ligand (0.024 mmol), and K_2CO_3 (0.4 mmol) in THF (2.0 mL). [b] Yield was determined by ^{1}H NMR using dibromomethane as the internal standard. [c] The ee value was determined by HPLC analysis on a chiral stationary phase.

Table 3 Cross-coupling of 3-bromo-isobenzofuranone with various aryl boronic acids[a,b,c]



[a] Reactions were carried out at 70 °C for 12 h by using 3-bromo-isobenzofuranone **1a** (0.3 mmol), aryl boronic acid (0.6 mmol), Ni catalyst (0.03 mmol), ligand (0.036 mmol), and K_2CO_3 (0.6 mmol) in THF (3.0 mL). [b] Isolated yield. [c] The ee value was determined by HPLC analysis on a chiral stationary phase.

Table 4 Cross-coupling of various 3-bromo-phthalides with phenylboronic acid[a,b]



[a] Isolated yield. [b] The ee value was determined by HPLC analysis on a chiral stationary phase.

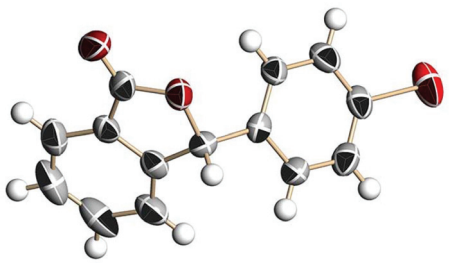


Fig. 1 X-ray crystallographic structure of **3f**.

thiophene (**3m**), pyridine (**3n**) and benzofuran (**3o**), were also successfully employed, albeit with reduced reaction yields.

Next, we assessed the substituents on the phenyl ring of 3-bromo-phthalides (Table 4). Although the enantioselectivities fluctuated with different substituents at different positions of the phenyl ring, they were at very good levels for most tested cases. However, methyl substitution at the 4-position, which is close to the reaction center, had a significant effect on enantioselective control, giving a low ee value of 7% (**3w**). In contrast to the substituent effect on arylboronic acid, electron-withdrawing substituents at the 5-position of the phenyl ring gave better reaction yields (**3p–3s**).

The newly formed stereogenic center of known structures shown in Tables 3 and 4 was assigned by comparison with the reported optical rotation data. In addition, the optically pure product **3f** was obtained by recrystallization and its absolute configuration was also confirmed by X-ray crystallography analysis (Fig. 1).[22] For other products, their stereochemistry was assigned as indicated based on the assumption of an analogous reaction pattern.

Conclusions

In summary, we have developed a nickel-catalyzed asymmetric Suzuki–Miyaura coupling reaction of racemic 3-bromo-phthalides and arylboronic acids for the efficient preparation of diverse chiral 3-aryl-phthalides. This protocol proceeds in a stereoconvergent manner, showing very good enantioselectivities for most tested cases. Both aryl and heteroaromatic boronic acids were competent coupling partners, and a number of active functional groups like halides (Cl and Br), ester and aldehyde were well tolerated.

Conflicts of interest

The authors declare there is no conflict of interest regarding the publication of this paper.

Acknowledgements

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22 CCDC 2061494 (**3f**)† contains the supplementary crystallographic data for this paper.