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Metal-Free Direct α-Selective Arylation of Boron Dipyrromethenes via Base-Mediated C−H Functionalization

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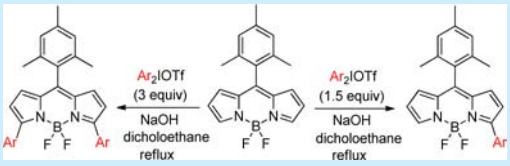
Supporting Information

ABSTRACT: A metal-free direct α-selective arylation of BODIPYs has been developed based on base-mediated C−H functionalization with easily accessible diaryliodonium salts, which provides a straightforward facile access to a variety of α-arylBODIPY dyes. The α-regioselectivity was confirmed by X-ray analysis, and was studied by DFT calculation. The resultant dyes show strong absorption and emission over a broad range of spectra tunable via the simple variation of the diaryliodonium salts.

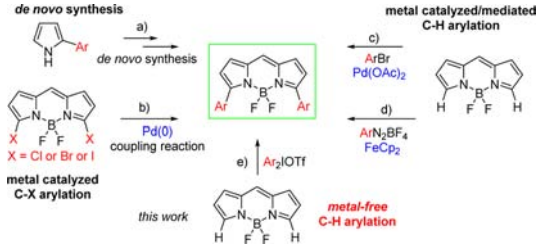


BODIPY (4,4′-difluoro-4-bora-3a,4a-diaza-*s*-indacene) dyes have found wide applications in highly diverse research fields,[1] for example, as labeling reagents and probes in biology[2] and as energy-transfer cassettes in material science,[3] due to their remarkable photophysical properties such as large molar absorptivity, sharp fluorescence emissions, high fluorescence quantum yields, and high photostability. These photophysical properties can be finely tunable via the structural variations based on their rich chemistry.[4,5] For example, the installation of aryl groups onto the α-position(s) of the BODIPY chromophore has been widely used to extend the π-conjugation of the chromophore and to achieve long-wavelength dyes.

Traditionally, most α-arylBODIPYs were generated either from de novo synthesis of α-arylpyrroles[6] (Scheme 1a) or from the transition-metal-catalyzed α-arylation on halogenated BODIPY dyes[7] (Scheme 1b). Later, Dehaen and co-workers[8] reported the improved efficient synthesis of α-arylBODIPYs based on palladium-catalyzed C−H activation of BODIPY chromophore (Scheme 1c). Recently, the first radical reaction on BODIPY by Dehaen and co-workers provided a direct access to α-arylBODIPYs using aryldiazonium salts mediated by ferrocene (Scheme 1d).[9] Nevertheless, these above elegant methods still required the assistance of metal catalyst or promoters.

Hypervalent iodine(III) compounds have recently been demonstrated as efficient reagents for a wide range of transformations.[10] These readily available diaryliodonium salts are nontoxic, bench stable, and highly reactive and have been applied for the regioselective electrophilic arylation of various nucleophiles in the presence of various transition metals or under metal-free conditions, for example, arylation of indoles with $Cu(OTf)_2$,[11a,b] or metal-free conditions[11c] and simple arenes with platinum, copper, or palladium salts.[11d−f] Herein we report a metal-free, highly regioselective, direct α-arylation of BODIPY chromophores with easily accessible diaryliodonium salts. The regioselectivity was confirmed by X-ray analysis and may come via a radical process. These resultant α-arylBODIPYs show strong absorption and emission over a broad range of spectra that are tunable via the simple variation of the diaryliodonium salts.

Scheme 1. Synthesis of α-ArylBODIPYs[a]



[a]From (a) de novo synthesis of 2-arylpyrroles, (b) transition-metal-catalyzed coupling reaction on 3,5-dihalogenoBODIPYs, (c) and (d) metal-catalyzed/mediated C−H arylation of the BODIPY core, and (e) the metal-free direct C−H Arylation of the BODIPY core with diaryliodonium salts presented in this work.

Initially, we attempted the reaction between BODIPY **2** and a stoichiometric amount of diphenyliodonium salt **3a** in 1,2-dichloroethane (Table S1). In the presence of 1.5 equiv of K_2CO_3 (entry 2), a major product was obtained in 13% isolated yield and was confirmed to be the α-arylBODIPY **1a** according to X-ray analysis (Figure 1a). In the absence of base, only a trace amount of **1a** was detected from this reaction (entry 1, Table S1). A set of common organic solvents and inorganic bases were studied to achieve the optimized reaction conditions (entries 3−11, Table S1). Among those, use of 1,2-dichloroethane as solvent and NaOH as base gave the best result (entry 10, Table S1). We also investigated the influence of reagent ratio on this reaction. The optimized reaction conditions were set to be 1.5 equiv of **3a** and NaOH with respect to BODIPY **2**, respectively, in refluxing 1,2-dichloroethane.

A further increase in the number of equivalents of **3a** decreased the yield of **1a** with the appearance of 3,5-diphenylBODIPY **4a** (Table S1). The optimized ratio of **3a** for the diarylation reaction

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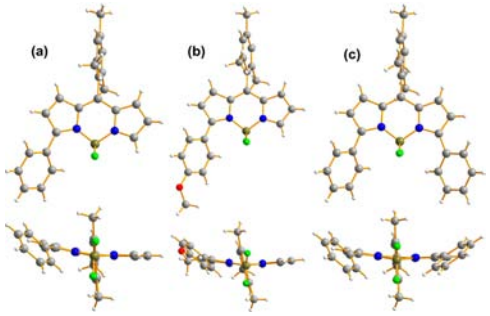
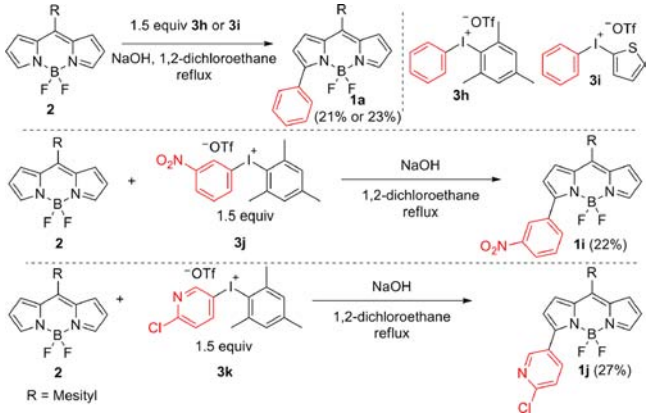


Figure 1. X-ray structures of **1a** (a), **1e** (b), and **4a** (c). Key: C, gray; H, light gray; O, red; N, blue; B, dark yellow; F, green.

was 3 equiv. At this ratio, 3,5-diphenylBODIPY **4a** was obtained regioselectively in 41% isolated yield (Scheme 2). The regioselectivity of this diarylation was also confirmed by X-ray analysis (Figure 1c). A further increase in the number of equivalents of **3a** only led to a decrease of the yield of **4a**. No tri- or multiphenylated products were observed.

To test the versatility of this α-arylation reaction, we further applied a set of diaryliodonium salts **3b**−**e** (Figure S1) containing either moderate electron-withdrawing groups (such as the chloro and bromo groups in **3b** and **3c**) or electron-donating substituents (such as the *tert*-butyl and methoxy groups in **3d** and **3e**) for this reaction. All of these functional groups were able to survive this reaction. Under the optimized reaction conditions, the desired α-arylBODIPYs **1b**−**e** and their corresponding 3,5-diaryBODIPYs **4b**−**e** were regioselectively obtained in 39−63% and 23−46% isolated yields with 1.5 and 3 equiv of diaryliodonium salts **3**, respectively (Scheme 2). Heteroaromatic hypervalent iodium salt, such as di(thiophene-2-yl)iodonium salt **3f**, was also suitable for this reaction and regioselectively generated the desired α-thienylBODIPY **1f** and 3,5-dithienylBODIPY **4f** in 37% and 23% isolated yields, respectively. Compared with **3a**−**f**, diaryliodonium salt **3g** with an *o*-methyl group showed lower reactivity in this reaction due to steric hindrance and gave **1g** in 17% yield. Besides *meso*-mesitylBODIPY **2**, unsymmetrical *meso*-H BODIPY **5** (Figure S1), possessing only one free α-position, was also applicable for this reaction, from which **1h** (Scheme 2) was

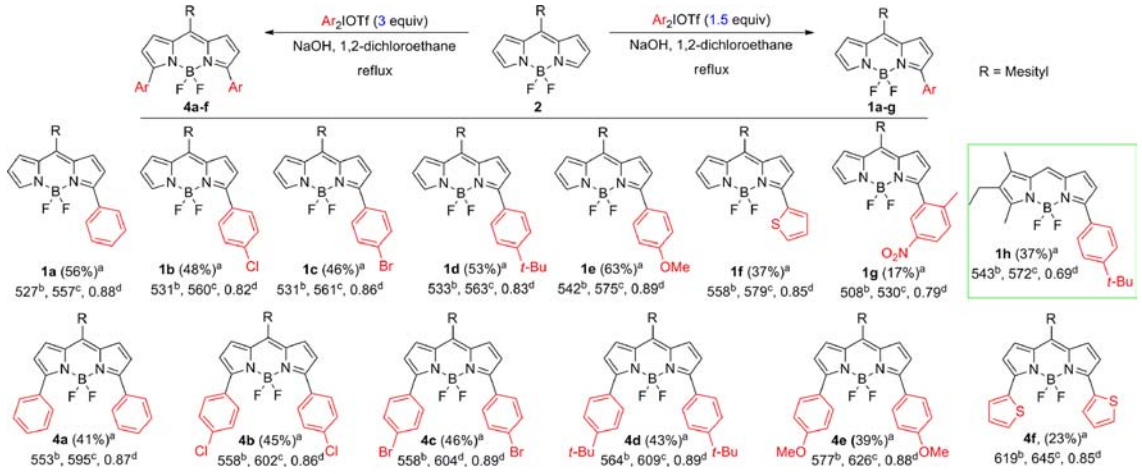
Scheme 3. Regioselective α-Arylation of BODIPY 2 with Unsymmetric Diaryliodonium Salts 3h−k



generated in a relatively lower (37%) yield with respect to that of *meso*-mesitylBODIPY **2**.

When unsymmetric diaryliodonium salts (**3h** and **3i**, Scheme 3) were used for this reaction, a high chemoselectivity, closely associated with the steric hindrance and electronic effects of the aryl groups, was observed. When **3h** containing phenyl and *meso*-mesityl groups was used for this reaction, only the less bulky phenyl group was installed onto the α-position of the BODIPY core. This result, however, did not follow the *ortho*-effect with sterically hindered salts as previously reported[12a−c] and further illustrated the delicate balance between steric and electronic effects.[12d] The use of **3i** containing both the phenyl and the thiophene groups for the reaction gave the same arylation product **1a** in a compatible yield. The chemoselectivity observed here was in good agreement with previously reported selectivities, and electron-poor aryl groups were transferred prefentially over electron-rich aryl groups under metal-free conditions.[12] These unsymmetric diaryliodonium salts provide alternative arylation reagents when the symmetric diaryliodonium salts were hard to access. For example, electron-poor aryl groups, such as 3-nitrophenyl and pyridium derivatives, were selectively installed on the BODIPY core from **3j** and **3k**, giving **1i** and **1j** in 22% and 27% yields, respectively (Scheme 3).

Scheme 2. Synthesis of Mono- and DiarylBODIPYs 1 and 4 from the Reaction of α-Free BODIPYs with Easily Accessible Diaryliodonium Salts 3 under Metal-Free Conditions



[a]Isolated yields. [b]absorption maxima. [c]emission maxima. [d]fluorescence quantum yield.

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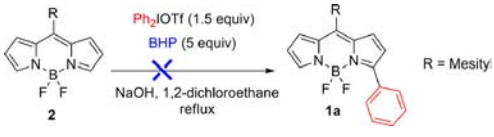
Crystals for BODIPYs **1a**, **1e**, and **4a** (Figure 1) suitable for X-ray analysis were obtained via the slow diffusion of petroleum ether into the dichloromethane solutions of these dyes under atmospheric pressure. As usual, each of these arylated BODIPYs show an almost planar structure for the BODIPY core (the central six-membered C_3N_2B ring with two adjacent five-membered pyrrole rings) with the plane defined by F−B−F atoms perpendicular to that of the BODIPY core. The dihedral angle between the *meso*-mesityl group and the BODIPY core is around 81°, 74°, and 87° for **1a**, **1e**, and **4a**, respectively. The dihedral angle between the α-aryl group(s) and the BODIPY core is 37°, 35°, and ~40° for **1a**, **1e**, and **4a**, respectively. The B−N distance for these BODIPYs is within 1.54−1.55 Å, which indicates the usual delocalization of the positive charge. In the solid state, there are multiple C−H···F intermolecular hydrogen bonds between F atoms and methyl hydrogens with the bond distance in the range of 2.07−2.84 Å (Table S2).

According to the mesomeric structures of BODIPY **2** (Figure S3), the 2,6-(β-) positions of the BODIPY core bear the least positive charge and should be most susceptible to electrophilic attack as demonstrated in the regioselective formylation, halogenation, sulfonation, and nitration reactions.[13] Surprisingly, this arylation reaction occurs regioselectively at the α-position of the BODIPY chromophore. No expected β-arylated product was detected. This interesting regioselectivity led us to further investigate the reaction mechanism for this reaction.

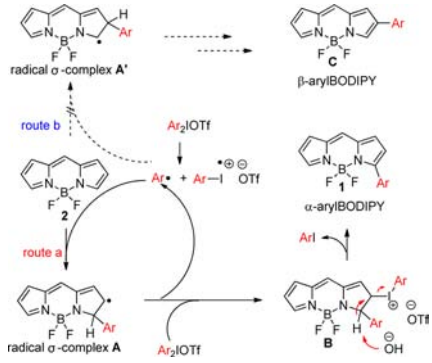
Since decomposition of diaryliodonium salts to generate aryl radicals has been disclosed in the literature,[14] we proposed that our regioselective α-arylation would come through a radical process. To test our hypothesis, a radical inhibitor, BHT (2,6-di-*tert*-butyl-4-methylphenol), was added into the reaction mixture (Scheme 4). No reaction was detected even at an extended reaction period. This indicates a possible radical reaction pathway for this α-arylation (route a, Scheme 5). It involves the generation of the aryl radical species from the decomposition of diaryliodonium salts **3** and its further reaction with BODIPY **2** at the α-position to form intermediate **A**. Subsequently, **A** reacts with diaryliodonium salts **3** to generate intermediate **B** and releases aryl radical species. In the final step, hydroxide anion (from the base) attacks the α-proton of **B** to restore the aromaticity of the pyrrolic unit to form target α-arylBODIPY **1** and release aryl iodide.

After considering the steric hindrance effect from the *meso*-mesityl group, theoretically, there are still two possible competitive radical reaction pathways available for this arylation reaction (routes a and b, Scheme 5). To understand the reason for the regioselective formation of α-arylBODIPY **1** instead of its competitive product (β-arylBODIPY **C**) as observed in the experiment, a computational study at the B3LYP/6-31G(d) level using the Gaussian 09 program was performed on the reaction of BODIPY **2** with phenyl radical, and the energy profiles are depicted in Figure 2. The formation of the transition state TS2 (route b) requires an activation energy of 13.5 kcal/mol, which is 3.3 kcal/mol higher than that required for the formation of transition state TS1 (route a). Furthermore, intermediate **A** is more stable (by 13.3 kcal/mol) than A′. Therefore, the calculated

Scheme 4. Influence of BHP on This Arylation Reaction



Scheme 5. Proposed Reaction Mechanism for the Regioselective α-Arylation of BODIPY 2 (Route a, with Solid Lines) and Its Possible Competitive Radical Reaction Pathway (Route b, with Dashed Lines) for the Regioselective Formation of β-ArylBODIPYs



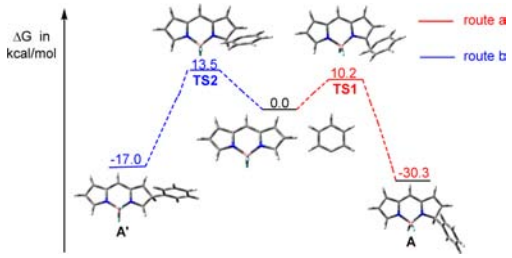


Figure 2. Free energy profiles for the two competitive radical reaction pathways (routes a and b in Scheme 5) in the radical reaction of BODIPY **2** and the in situ generated phenyl radical at 298.15 K: structures of transition states TS1 (route a) and TS2 (route b), structures of the intermediates A (route a) and A′ (route b), and their corresponding activation free energies.

energy profiles are in good agreement with the experimental results, which clearly indicate that the formation of α-arylBODIPY **1** (via route a) is energetically more favorable than that of β-arylBODIPY **C** (via route b). Possible reaction at the *meso*-position (route c in Scheme S2) was also investigated. The energies of both the transition state and intermediate **A**″ are also higher than those at the *a*-position. Further attempts to install an aryl group on the BODIPY *meso*-position with 3,5-disubstituted BODIPYs **6** and **7** failed (Scheme S2).

Photophysical properties of these resultant α-arylBODIPYs were investigated in dichloromethane and are summarized in Table S3. As demonstrated in Figure 3, α-arylation led to a

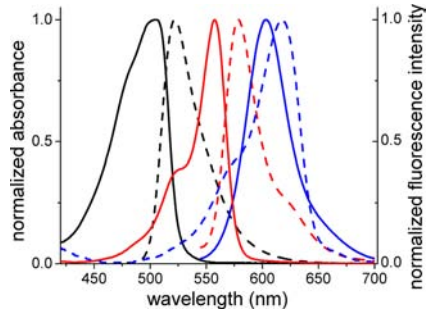


Figure 3. Overlaid normalized absorption (solid lines) and fluorescence emission (dashed lines) spectra of **2** (black), **1f** (red), and **4f** (blue) in dichloromethane at room temperature.

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significant red-shift of the absorption and emission maxima with respect to the starting BODIPY **2**. In comparison to **2**, monoarylation (BODIPYs **1a**−**f**) generally led to an around 30−60 nm red-shift of the absorption and emission maxima, while diarylation (BODIPYs **4a**−**f**) provided an additional red-shift of the absorption and emission maxima (up to 60 nm) with respect to the corresponding monoarylation ones. These mono- and di-α-arylBODIPYs all show intense fluorescence emission ($0.7 < \Phi < 0.9$). As shown in Figure S4, the absorption and emission maxima can be easily tuned via the variation of the electronic properties of the aryl group(s) in the diaryliodonium salts **3**: the increase of the electron density of the aryl group(s) led to a gradual red-shift of the spectra.

In conclusion, a general and facile synthesis of a set of mono- and di-α-arylBODIPYs was developed on the basis of a base-mediated direct C−H α-arylation in refluxing 1,2-dichloroethane with easily accessible diaryliodonium salts under metal-free conditions. This regioselective α-arylation reaction may come through a radical process. The resultant α-arylBODIPYs showed strong absorption and intense fluorescence emission over a broad range of the spectra and may be easily tuned via the variation of diaryliodonium salts.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b03706.

Experimental details, tables, and additional spectra (PDF)
X-ray data for **1a**, **1e**, and **4a** (CIF)

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Notes

The authors declare no competing financial interest.

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