<u>LETTERS</u>

Structurally Diverse α -Substituted Benzopyran Synthesis through a Practical Metal-Free C(sp³)–H Functionalization

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Supporting Information

ABSTRACT: A trityl ion-mediated practical C–H functionalization of a variety of benzopyrans with a wide range of nucleophiles (organoboranes and C–H molecules) at ambient temperature has been disclosed. The metal-free reaction has an excellent functional group tolerance and high chemoselectivity and displays a broad scope with respect to both benzopyran and nucleophile partners, efficiently affording a collection of benzopyrans bearing diverse skeletons and α functionalities in one step.



B enzopyrans are one of the most common structural motifs spread across biologically active natural products and synthetic pharmaceuticals.¹ For example, benzopyrans comprising (iso)chromans and (iso)chromenes bearing diverse α functionalities (aryl, vinyl, and alkyl) have been extensively used as antioxidants (e.g., vitamin E) and pharmaceuticals possessing antipsychotic, antibacterial, antifungal, antiviral, and anticancer activities (Figure 1).¹ Besides that, α -functionalized benzopyrans have also found a wide range of applications in other high-tech applications like photochromic lenses and sensitizers in solar cells.²



Figure 1. Representative α -substituted benzopyrans in human technology.

Inspired by the significance of these compounds in modern pharmacology, extensive efforts have been devoted to their synthesis. While the traditional strategies relying on reactive functional group transformations have found wide utility in chemical synthesis, the installation of the functionalities usually requires multiple and unproductive steps.³ On the other hand, precise and direct C–H functionalization of ethers with carbon components presents an atom- and step-economic strategy without prior incorporation of activating groups.⁴ Since Li's pioneering study in 2006, the synthesis of α -substituted benzopyran derivatives through direct sp³ C-H functionalization has attracted considerable attention.^{5,6} In the presence of suitable metals, oxidants including 2,3-dichloro-5,6-dicyano-1,4benzoquinone (DDQ), organic peroxides, N-hydroxyphthalimide (NHPI), 2,2,6,6-tetramethylpiperidine-1-oxoammonium tetrafluoroborate $(T^+BF_4^-)$, and $Na_2S_2O_8$ were reported to promote the cross-dehydrogenative coupling (CDC) of isochromans with several types of C-H nucleophiles including reactive carbonyl compounds, arylacetylene, and electron-rich aryl rings including indole and anisole. Despite great innovation, each method only focused on a single class of the nucleophile, and the scope with respect to benzopyran is largely restricted to xanthene and isochroman moieties. Moreover, known methods rely heavily on the employment of a metal additive, usually requiring high temperature, neat conditions, and long reaction time, all of which are generally disadvantageous for developing asymmetric variants. With respect to the synthetic utility, the specific structures of employed C-H nucleophiles restrict the integrated pattern of functionalities in the α -position of benzopyrans. Therefore, the majority of structures exhibited in Figure 1 could not be concisely achieved through these methods. Recently, Muramatsu and Li disclosed a one-pot oxidative coupling of isochroman with Grignard reagents, affording diverse α substituted derivatives in high efficiency.⁷ However, the employment of Grignard reagents might bring about unfavorable regioselectivity and functional group intolerance during the manipulation of highly functionalized substrates. Highly functionalized organometallic reagents might also not be readily accessible. Therefore, the development of a practical and mild metal-free method for direct C-H functionalization of a variety

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Organic Letters

of benzopyrans with a wide range of carbon nucleophiles is highly desired.

We focused our attention on trityl ions as the oxidant for benzopyran oxidation for the following reasons: trityl ions are stable, nontoxic, easily handled, and readily prepared from trityl chloride and the corresponding acid (e.g., $HClO_4$ or HBF_4) in a single step.^{8a} Moreover, trityl ions were reported to mediate benzyl ether cleavage and the C–H functionalization of 1,3-dioxolane.^{8b–d} Very recently, we disclosed that the combination of Ph₃CCl and 1 equiv of GaCl₃ can promote C-H functionalization of a variety of ethers with potassium phenylethynyltrifluoroborate.⁹ Although isochroman was a suitable substrate for the specific nucleophile, the oxidation system proved to be ineffective for alkylethynylboranes and other types of organoboranes, such as aryl-, vinyl-, benzyl-, and allylboranes, as well as typical C-H nucleophiles like reactive carbonyls and aryl rings.¹⁰ While the origin of the limited scope was not clear, the different counterion effect of the trityl ion on the coupling efficiency observed in the previous study encouraged us to explore the suitable oxidation system for the C-H functionalization of benzopyrans with a wide range of nucleophiles.^{8d}

Given the paramount importance of α -arylated benzopyrans, the arylation of isochroman 1a with potassium (4methoxyphenyl)trifluoroborate 2a was initially selected as a model reaction for the optimization (Table 1). A variety of trityl

Table 1. Screen for the $Oxidant^a$



^{*a*}Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), and oxidant (0.2 mmol) in CH₂Cl₂ (2.0 mL) at rt. ^{*b*}Isolated yield. ^{*c*}Oxidants including DDQ, PhI(OAc)₂, K₂S₂O₈, CAN, MnO₂ and TBHP/CuBr₂. Tf = trifluoromethanesulfonyl.

salts bearing different counterions were examined, and reaction optimization experiments identified Ph_3CClO_4 in CH_2Cl_2 at room temperature in 2 h as ideal conditions (entries 1–6, Table 1). Other common oxidants including tropylium cation $(C_7H_7BF_4)$, DDQ, PhI(OAc)₂, Na₂S₂O₈, CAN (cerium ammonium nitrate), MnO₂, and TBHP (*tert*-butyl hydroperoxide)/CuBr₂ failed to effect the coupling (entries 7 and 8 and Table S1 in the Supporting Information).

The reaction proved general for a broad range of organoboranes, allowing for efficient coupling with potassium aryl-, vinyl-, alkynyl-, benzyl-, and allyltrifluoroborates (Table 2). Boronic acids (**3ab**, **3ga**, and **3ia**) and boronate ester (**3ac**) are also competent components, providing results comparable to those of the potassium trifluoroborate (**3a**, **3g** and **3i**). The employment of organoboranes as nucleophiles is classically confined to π -rich aryl moieties or relies on transition metals or





^{*a*}The reaction was carried out with **1a** or **4** (0.2 mmol), **2** (0.4 mmol), and Ph_3CClO_4 (0.2 mmol) in CH_2Cl_2 (2.0 mL) at 0 °C or rt in 2 h. ^{*b*}Boronic acid as nucleophile. ^{*c*}Diethyl (*p*-methoxyphenyl)boronate as nucleophile. ^{*d*}Reaction at 40 °C.

Lewis acids.¹¹ As shown in Table 2, the metal-free reaction is efficient not only for the π -rich aryl (3a,b) and heteroaryl borates (3e) but also for π -neutral (3c) and π -deficient (3d) arylboranes, though electron-poor 2-pyridinyl borate (3f) failed to give the desired product. The C–H functionalization strategy does not require any additive and thus alleviates potential chemoselectivity problems that usually arise from the conventional Lewis acid initiated methods for electrophile formation through acetal collapse. Consequently, the functional group compatibility is excellent, with halogens (3d, 3j, and 3o), benzyl ether (3l), olefins (3g, 3h, and 3p), and alkynes (3i–1) well-tolerated for further manipulations.

Next, we examined the scope of benzopyrans (Table 2). Structurally and electronically varied isochromans 4a-f reacted smoothly with potassium aryltrifluoroborate 2a. Electron-rich isochromans, which were expected to be much less reactive than isochroman 1a, also afforded products in good yields (5c-e).^{Sb,7} Isothiochroman (4g) reacted well under the standard conditions. 1*H*-Isochromene (4h) was subjected to decomposition under the oxidation conditions, which could be ascribed to an incompatibility of the enol ether moiety toward the Lewis acidity of the trityl ion.¹² 2*H*-Chromenes also proved to be competent substrates, with electronically varied substrates 5i-m well tolerated. The reaction is highly regioselective, delivering predominantly C_2 -addition products, and no double functionalization was observed. High efficiency was also achieved when π -neutral (2c) and π -deficient (2d) arylboranes were applied (5n

and **50**). In consideration of a variety of known protocols utilizing the unsaturation in 2*H*-chromene as a reactive handle for further functionalization, the direct access to α -substituted chromenes provides excellent opportunities to develop a structurally and stereochemically diverse library of chroman-like compounds through diversity-oriented synthesis.¹³ Xanthene (**5p**) and benzoxathiole (**5q**) also worked well under the standard conditions.

The CDC of isochromans with C–H nucleophiles typically required the employment of metal additives under harsh conditions for reaction completion,⁵ and each condition is only suitable for a single class of the nucleophile. The mild metal-free oxidation system encouraged us to explore the scope of CDC reactions by using the trityl ion as the sole agent (Table 3). The



^{*a*}The reaction was carried out with **1a** or **4** (0.2 mmol), **6** (0.4 mmol), and Ph₃CClO₄ (0.2 mmol) in CH₂Cl₂ (2.0 mL) at 0 °C or rt in 2 h. ^{*b*}**6** was added once the oxidation process was complete. ^{*c*}Na₂HPO₄ (0.4 mmol) was added. ^{*d*}1.0 mmol of aldehyde used.

arylation of 1a with anisole proceeded smoothly at 0 °C in 2 h to deliver 7a in a yield comparable to that reported by Todd through DDQ/CuCl₂-mediated coupling at 100 °C after 36 h.^{5b} 3-Methoxyanisole, a challenging substrate for the DDQ system, afforded the desired 7b in 15% yield.^{5b} Trityl ion mediated mild conditions allowed a variety of ketones (7c-i) including volatile acetone (7h) to participate in the coupling efficiently. The aldehyde component was next studied. However, when propanal 6k was subjected to the standard conditions, no desired 7k was detected, with aldehyde self-condensation identified as the major pathway probably because of the Lewis acidity of the trityl ion.¹² After extensive investigation of a variety of basic additives, Na₂HPO₄ was finally found to be essential to suppress the undesired pathway, affording 7k in 73% yield (see Table S2, Supporting Information). Under the optimized conditions, both linear aldehydes like acetaldehyde (7j) and pentanal (7l) and sterically hindered branched ones like 7m and 7n joined in the coupling efficiency.¹⁴ Additionally, the modified condition

adapted to α,β -unsaturated aldehydes, yielding predominantly γ -alkylated products in good efficiency (7 $\mathbf{o}-\mathbf{q}$). Electronically varied isochromans and 2*H*-chromenes were competent substrates for CDC reactions with representative C–H nucleophiles like anisole, acetophenone, and propanal (8 $\mathbf{a}-\mathbf{h}$).

The trityl ion mediated C–H oxidation is typically believed to undergo direct hydride abstraction or formal hydride transfer involving an initial single electron transfer (SET) (Figure 2).¹⁵



Figure 2. Mechanistic analysis for $\mathrm{Ph}_3\mathrm{CClO}_{4^{\text{-}}}\mathrm{mediated}$ benzopyran oxidation.

The reaction efficiency was not influenced when the C–H oxidation was conducted prior to the addition of **2a**, suggesting that the organoborane might not participate in the oxidation process. Substrates displayed a kinetic isotope effect, indicating the C–H cleavage involved in the rate-determining step. Radical trapping experiments were performed, in which the coupling of **1a** with **2a** was not affected by 1 equiv of 2,2,6,6-tetramethylpiperidin-1-yloxy (TEMPO) or 2,6-di-*tert*-butyl-4-methylphenol (BHT). The observation suggested that a radical intermediate might not be involved in the reaction. While we cannot conclude which of the two possibilities might be viable at this time, we would like to reemphasize that DDQ-mediated C–H oxidation, typically involving a formal hydride transfer initiated by a SET,¹⁶ could be dramatically suppressed in the similar radical trapping experiments.^{5b,17}

In conclusion, a metal-free C-H functionalization of benzopyrans using a readily available trityl ion as the sole oxidizing agent has been developed. The reaction proceeds smoothly under ambient temperature with excellent chemoselectivity, and it exhibits a broad scope with respect to both benzopyran ((iso)chroman and chromene) and nucleophile (organoborane and C-H component) partners with high functional group tolerance. The integrated pattern of functionalities in the α -position of benzopyrans is broad, including aryl, vinyl, alkynyl, benzyl, allyl, and alkyl moieties, which have potential for further functional handles. We envision that this avenue will not only allow a facile and rapid access to series of multiple benzopyrans through "structural core diversification" strategy to discover biologically significant small molecules but also provide a valuable platform for further efforts toward inventing catalytic asymmetric C-H functionalization of benzopyrans.

ASSOCIATED CONTENT

Supporting Information

Experimental details and spectral data for new compounds. This material is available free of charge via the Internet at http://pubs. acs.org.

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Notes

The authors declare no competing financial interest.

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