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Photochemical Boronate Rearrangement Enables the One-Pot Synthesis of 2,4-Difunctionalized 2*H*-Chromenes

Chenyang Xu,[#] Yixin Zhang,[#] and Yiyun Chen*

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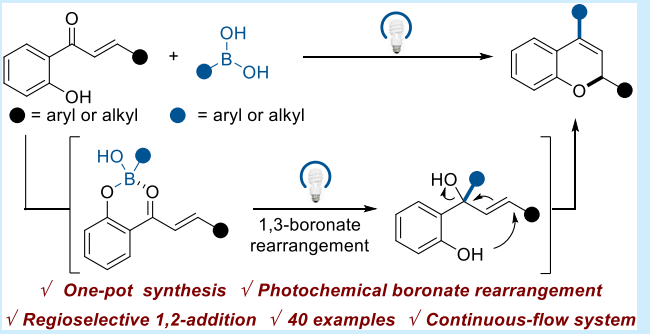
ABSTRACT: 2*H*-Chromenes are privileged pharmaceutical scaffolds, yet their synthesis typically requires multistep sequences or harsh conditions. We report a one-pot, visible-light-mediated strategy that directly converts 2′-hydroxychalcones and organoboronic acids into diverse 2,4-disubstituted 2*H*-chromenes. This approach leverages a photochemical 1,3-boronate rearrangement to achieve highly regioselective 1,2-addition to the *α*,*β*-unsaturated ketone moiety of 2′-hydroxychalcones, effectively diverting from traditional 1,4-addition pathways. The method provides modular access to 40 examples, notably including the synthetically challenging 2-alkyl-4-aryl motif. Demonstrating broad functional group compatibility, the protocol was successfully implemented in a continuous-flow system, achieving an 85% reduction in reaction time and facilitating gram-scale synthesis.



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The efficient synthesis of bioactive heterocycles from simple starting materials remains a central challenge in synthetic chemistry.[1] Among these privileged structures, substituted 2*H*-chromenes constitute a fundamental class of scaffolds, prevalent in pharmaceuticals, agrochemicals and natural products due to their diverse biological activities.[2] Representative examples include Myristinin A, an antifungal and DNA polymerase *β* inhibitor;[3] and Acolbifene, a selective estrogen receptor modulator used in breast cancer therapy (Scheme 1a).[4] Despite their importance, the limited natural availability of functionalized 2*H*-chromenes necessitates efficient synthetic methodologies.

Conventional strategies typically involve the late-stage functionalization of preconstructed 2*H*-chromene cores,[5] which is often effective only for C2-substitution and suffers from multistep substrate preparation.[6] While cyclization-based strategies can access diverse patterns, they generally require harsh conditions, metal catalysts, or specialized precursors.[7] Notably, organoboronic acid−based Petasis-type reactions remain constrained;[8] they typically depend on specific alkenylboronic reagents and afford only 2-substituted derivatives. Consequently, a modular approach to access various three major 2,4-disubstitution patterns—particularly the elusive 2-alkyl-4-aryl motif—remains an unmet need in the field.

In recent years, the transformation of boronic acids under photochemical conditions has been extensively studied and applied.[9] Inspired by our previous work on photochemically active tetracoordinate boron species and visible-light-driven boronate rearrangement,[10] we sought to overcome these limitations via a conceptually distinct pathway. Herein, we disclose a strategy that directly converts readily available 2′-hydroxychalcones and organoboronic acids into structurally diverse 2,4-difunctionalized 2*H*-chromenes under mild, visible-light-induced conditions. This transformation proceeds through a photoactivated six-membered boronate intermediate, enabling regioselective 1,2-addition/cyclization cascade. Critically, this method favors the challenging 1,2-regioselectivity by suppressing the inherent preference for 1,4-addition to *α*,*β*-unsaturated ketones. Operating without classical strong nucleophiles or exogenous Lewis acids, this reaction provides streamlined access to 2-alkyl-4-aryl motifs and is readily scalable via continuous-flow, achieving an 85% reduction in reaction time.

We initiated investigation by reacting 2′-hydroxychalcone (**1a**) and *p*-tolylboronic acid (**1b**, 3.0 equiv) in trifluoroethanol (TFE) under blue LED irradiation, which afforded the desired 2,4-disubstituted 2*H*-chromene (**1**) in 56% yield (Table 1, entry 1). A screening of bases revealed that mild inorganic additives, such as $NaHCO_3$ and NaOAc were beneficial, providing yields of 61% and 58%, respectively (entries 2−3). In contrast, organic bases like DMAP and DABCO suppressed the transformation (entries 4−5), indicating that inorganic bases effectively modulate the protic solvent environment

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Scheme 1. Photochemical Boronate Rearrangement Enables the One-Pot Synthesis of 2,4-Difunctionalized 2*H*-Chromenes

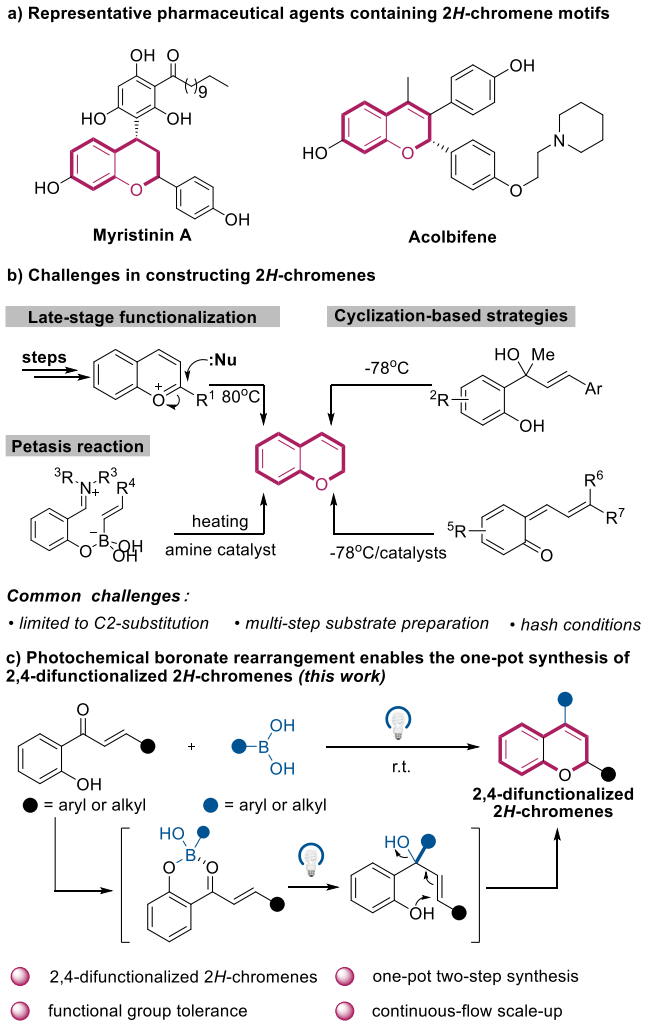
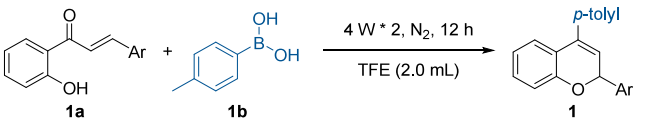


Table 1. Reaction Optimization



Ar = 2,6-dimethylphenyl

Entry	Conditions[a]	1a conv. (%)[b]	Yield of 1[b] (%)
1	None	>95	56
2	$NaHCO_3$ (2.0 equiv)	>95	61
3	NaOAc (2.0 equiv)	>95	58
4	DMAP (2.0 equiv)	>95	38
5	DABCO (2.0 equiv)	>95	31
6[c]	DCM	26	<5
7[c]	EtOH	88	<5
8	$NaHCO_3$ (1.5 equiv)	>95	68(66)
9[d]	20 W Kessil	>95	61
10[d]	*w/o* light	10	<5

[a]Reaction conditions: **1a** (0.10 mmol, 1.0 equiv), **1b** (0.30 mmol, 3.0 equiv) and base in 2.0 mL of TFE under nitrogen with blue LEDs irradiation at 25 °C for 12 h. [b]Conversion and yields were determined by ^{1}H NMR analysis, and isolated yields are in parentheses. [c]Condition of entry 2. [d]$NaHCO_3$ (0.15 mmol, 1.5 equiv).

without interfering with the photochemical pathway. The choice of solvent proved critical; the use of DCM or EtOH completely shut down product formation (entries 6−7). This underscores the essential role of TFE, which likely promotes the generation of the allylic cation from the allylic alcohol intermediate through its high ionizing power and hydrogen-bonding ability.

Further optimization using 1.5 equiv of $NaHCO_3$ delivered the target 2*H*-chromene in 68% yield (66% isolated, entry 8; see Tables S1−S2 for comprehensive details). Notably, increasing the irradiation intensity with a 20 W Kessil lamp did not improve the outcome (61% yield, entry 9),[11] confirming that the reaction performs optimally under mild visible-light conditions (entry 10).

With optimized conditions, we evaluated the scope of boronic acids (Scheme 2). The reaction displayed robust compatibility with a wide array of aryl boronic acids. Substrates bearing electron-donating alkyl groups reacted smoothly to provide chromenes **1**−**4** in 53−66% yields. Heteroatom-containing substituents, including methoxy, methylthio, and acetoxy groups, were well-tolerated (**5**−**7**, 40−59%), as were sterically demanding extended π-systems such as biphenyl and naphthyl derivatives (**8**−**9**). Notably, the method remained chemoselective in the presence of reactive protic groups (**10**−**12**), which often require protection in traditional organometallic additions.[12] Electron-deficient aryl boronic acids were also compatible, albeit with slightly attenuated yields (**13**−**15**, 45−50%). The position of the substituent had minimal impact on efficiency, as evidenced by the successful incorporation of *meta*-substituted methyl, methoxy, and hydroxyl groups (**16**−**18**). Highlighting the potential for late-stage functionalization of complex architectures, a tyrosine-derived boronic acid was successfully coupled to afford product **19** in 66% yield (1:1 *d.r.*).

A significant feature of this photochemical manifold is its ability to accommodate alkyl boronic acids, which are often challenging in Petasis-type transformations due to the lower stability of the corresponding boronate intermediates.[13] Linear alkyl chains, ranging from methyl to *n*-hexyl (**20**−**22**), were incorporated in 42−56% yields. Furthermore, alkyl boronic acids tethered to ester, aryl, and alkenyl moieties (**23**−**25**) proved to be viable partners. Of particular note, the use of cyclopropylmethyl boronic acid afforded the desired product **26** in 59% yield without ring-opening, demonstrating the mild nature of the radical-free or 'in-cage' migration pathway and its compatibility with strained carbocyclic systems. Collectively, these results establish the strategy as a versatile and modular platform for assembling structurally diverse 2*H*-chromenes.

We next turned our attention to the scope of the 2'-hydroxychalcone derivatives (Scheme 3). Parent 2'-hydroxychalcone gave 2*H*-chromene **27** in 53% yield. While such substrates typically yield mixed 1,2-/1,4-addition products with classical organometallics,[14] our photochemical rearrangement provides exclusive 1,2-selectivity under mild conditions, tolerating diverse electronic and steric variations. Electron-donating groups and halogen atoms were all compatible, affording products **28**−**37** in synthetically useful yields (41−68%). Furthermore, extended π-systems, such as the naphthalene-derived substrate were successfully transformed into the product **38** (40% yield).

The most significant highlight of this manifold is its ability to access the previously elusive 2-alkyl-4-aryl-2*H*-chromene motif.[15] By employing 4-alkyl-substituted enones, we success-

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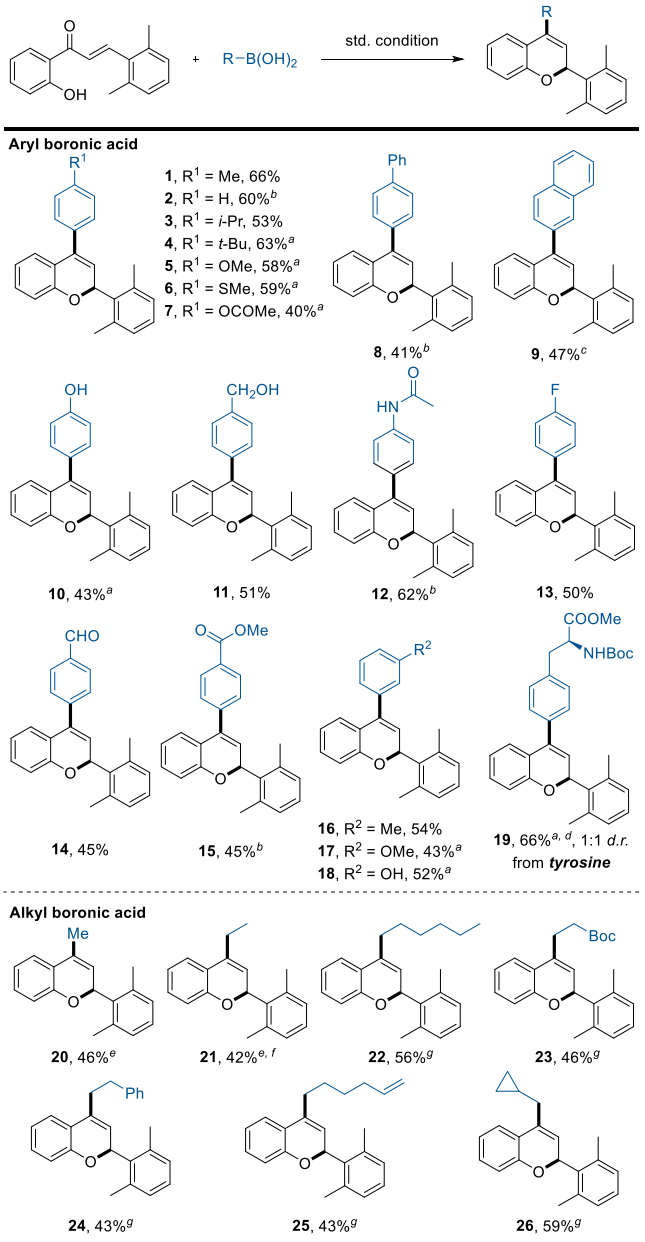
Scheme 2. Substrate Scope of Boronic Acids

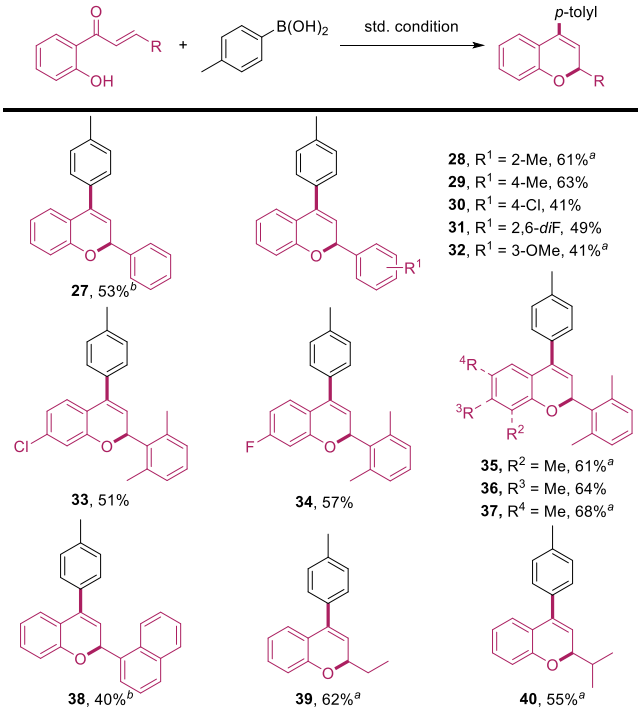


[a]Reaction conditions: 20 W, 456 nm. [b]Reaction time: 24 h. [c]40 W, 456 nm. [d]2.0 equiv of organoboronic acid. [e]20 W, 456 nm, *w/o* $NaHCO_3$, 12 h. [f]Stirred at 40°C for 2 h after 12 h light reaction. [g]20 W, 456 nm, *w/o* $NaHCO_3$, 24 h.

fully delivered products **39** and **40**, substitution patterns that are notoriously difficult to reach via conventional Petasis reactions or allylic alcohol cyclizations due to the limited availability and instability of the requisite precursors (Table S4). This achievement, alongside the streamlined synthesis of 2-aryl-4-aryl and 2-aryl-4-alkyl congeners, demonstrates that our platform uniquely enables the modular assembly of diverse 2,4-disubstituted chromene patterns from simple, commercially available precursors. This methodology significantly expands the accessible chemical space for this privileged pharmacophore.

To elucidate the underlying principles of this transformation, we conducted a series of spectroscopic and control experiments (Scheme 4). Initial UV−vis studies of chalcone **1a** and

Scheme 3. Substrate Scope of Chalcone Derivatives



[a]Reaction conditions: 20 W, 456 nm. [b]24 h.

boronic acid **1b** in TFE revealed a significant bathochromic shift extending beyond 550 nm, a phenomenon notably more pronounced than in EtOH (Scheme 4a). This suggested the formation of a photoactive complex promoted by the fluorinated solvent. The existence of a tetracoordinated boronate species was corroborated by *in situ* ^{11}B NMR spectroscopy, which displayed a characteristic upfield signal at δ 7.5 ppm. The association constant (K_a) was determined to be 25.5 M^{-1} (Figure S3). Interestingly, while electron-deficient boronic acids enhance complexation, excessively high binding constants were found to correlate with reduced yields, suggesting an optimal window of complex stability is required for efficient productive migration (Figures S4−S12).

To delineate the stages of the one-pot cascade, allylic alcohol **41**—the putative intermediate of the 1,2-addition—was subjected to the reaction conditions. In the absence of light, **41** successfully underwent cyclization to afford 2*H*-chromene **42** in 53% yield (Scheme 4b). This confirms the 1,2-addition as the light-demanding step and cyclization as light-independent. Excess boronic acid **1b** increased the cyclization yield to 70% (see SI), supporting its dual role in both initial complexation and Lewis acid-assisted carbocation formation.

The nature of the photoactivated migration was further probed (Scheme 4c). The addition of BHT had no impact on the yield, while TEMPO resulted in only a marginal decrease. More tellingly, the use of cyclopropylmethyl boronic acid afforded the addition product **26** (59%) without detectable ring-opening.[16] The experimental evidence strongly suggests that the 1,2-addition does not involve long-lived, freely diffusing radical intermediates. However, the involvement of a triplet-state species was supported by quenching studies; the reaction yield dropped significantly to 42% under an O_2 atmosphere, accompanied by the detection of singlet oxygen using α-terpinene as a probe (Scheme 4d).[17] Furthermore, the isolation of a 1,4-addition byproduct (10% yield) suggests a

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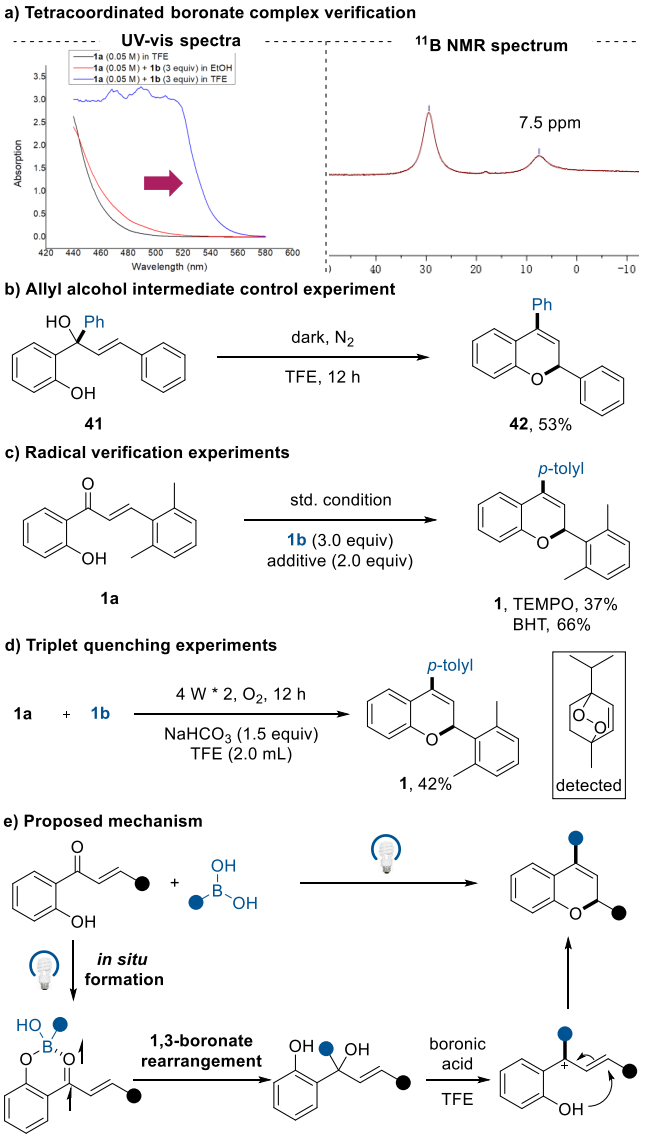
Scheme 4. Mechanistic Study

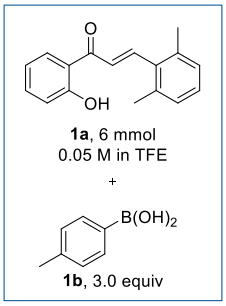


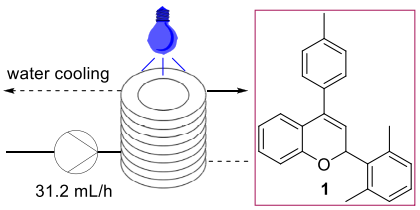
competitive, spin-separated 'in-cage' 1,5-migration pathway (see SI for detailed byproduct analysis). Collectively, these data support a mechanism involving a triplet-excited tetracoordinated boronate that undergoes a concerted or 'in-cage' 1,3-migration, followed by a Lewis acid-assisted cyclization.

Based on the aforementioned experimental evidence, we propose a plausible mechanism for this transformation (Scheme 4e). The process initiates with the condensation of 2'-hydroxychalcone and the organoboronic acid to form a six-membered cyclic tetracoordinated boronate complex. This intermediate is stabilized by a covalent B−O bond with the phenolic hydroxyl group and a coordinative B−O interaction with the carbonyl oxygen.[18] Upon visible-light irradiation, the complex is promoted to a triplet excited state, triggering an intramolecular 1,3-boronate rearrangement.[10a,19] This regioselective migration yields an allylic alcohol intermediate. In the presence of TFE—a solvent characterized by high ionizing power—and assisted by the Lewis acidity of the excess boronic acid, the intermediate undergoes dehydration to generate a stabilized allylic carbocation. Subsequent intramolecular nucleophilic attack by the phenolic oxygen affects cyclization, furnishing the final 2*H*-chromene scaffold. This visible-light-induced cascade provides a regioselective solution to α,β-unsaturated ketone functionalization, bypassing the need for the harsh conditions or exogenous additives required by prior methods.

To demonstrate the practical utility and potential for industrial translation of this protocol, we implemented a continuous-flow system.[20] Flow photochemistry offers distinct advantages, including enhanced irradiation homogeneity, improved safety profiles, and straightforward process intensification. Using a solution of chalcone **1a** and *p*-tolylboronic acid **1b** in TFE, the reaction was conducted in a flow photoreactor under 20 W Kessil LED irradiation at a flow rate of 31.2 mL/h (Scheme 5). Over a 5-h period, 120 mL of the

Scheme 5. Continuous-Flow System Scale up





	Mp	Isolated yield	Productivity
Flow (5 h)	1.02 g	52%	211 mg/h
Batch (36 h)	831.7 mg	42%	23 mg/h

reaction mixture was processed, affording 1.02 g of the desired product **1** (52% isolated yield), corresponding to a productivity of 211 mg/hour. Notably, the transition to a flow manifold reduced the reaction time by approximately 85% compared to the batch system while maintaining a comparable yield. These results demonstrate that process intensification significantly enhances the efficiency of this transformation. The combination of scalability, metal-free conditions, and mild reaction parameters positions this method as a robust and industrially relevant platform for heterocycle synthesis.

In summary, we have developed a visible-light-induced, one-pot synthesis of 2*H*-chromene that overcomes long-standing regiochemical challenges. By leveraging a photoactivated tetracoordinate boronate complex, this method achieves highly regioselective 1,2-addition to α,β-unsaturated ketones, significantly suppressing traditional 1,4-addition pathways. The protocol provides modular access to diverse 2,4-difunctionalized chromenes, notably including the elusive 2-alkyl-4-aryl motif. The utility of this strategy is further demonstrated by a continuous-flow manifold, which enables gram-scale synthesis with an 85% reduction in reaction time. Collectively, this photochemical boronate rearrangement offers a robust and sustainable platform for diversifying privileged heterocyclic libraries in medicinal chemistry.

■ ASSOCIATED CONTENT

Data Availability Statement

The data underlying this study are available in the published article and its Supporting Information.

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.6c00390.

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Experimental procedures, reaction optimization, mechanistic studies, characterizations and copies of NMR spectra. (PDF)

AUTHOR INFORMATION

Corresponding Author

Yiyun Chen − *State Key Laboratory of Chemical Biology, Shanghai Institute of Organic Chemistry, University of Chinese Academy of Sciences, Chinese Academy of Sciences, Shanghai 200032, China; School of Physical Science and Technology, Shanghai Tech University, Shanghai 201210, China; School of Chemistry and Material Sciences, Hangzhou Institute for Advanced Study, University of Chinese Academy of Sciences, Hangzhou 310024, China;* orcid.org/0000-0003-0916-0994; Email: yiyunchen@sioc.ac.cn

Authors

Chenyang Xu − *State Key Laboratory of Chemical Biology, Shanghai Institute of Organic Chemistry, University of Chinese Academy of Sciences, Chinese Academy of Sciences, Shanghai 200032, China*

Yixin Zhang − *State Key Laboratory of Chemical Biology, Shanghai Institute of Organic Chemistry, University of Chinese Academy of Sciences, Chinese Academy of Sciences, Shanghai 200032, China*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.orglett.6c00390

Author Contributions

#C.X. and Y.Z. contributed equally to this work.

Notes

The authors declare no competing financial interest.

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