EDGE ARTICLE

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Photoredox-catalyzed stereo- and regioselective vicinal fluorosulfonyl-borylation of unsaturated hydrocarbons†

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There has been considerable research on sulfur(VI) fluoride exchange (SuFEx) chemistry, which is considered to be a next-generation click reaction, and relies on the unique balance between reactivity and stability inherent in high valent organosulfur. The synthetic versatility of the bifunctional handles containing the fluorosulfonyl group presents great synthetic value and opportunity for drug discovery. However, the direct photoredox-catalyzed fluorosulfonyl-borylation process remains unexplored and challenging due to its system incompatibility and limited synthetic strategies. Herein, we developed a sequential photocatalytic radical difunctionalization strategy for the highly efficient stereoselective synthesis of vicinal fluorosulfonyl borides (VFSBs) with an integrated redox-active SO₂F radical reagent. The VFSBs acted as orthogonal synthons, and were subjected to a range of convenient transformations via the cleavage of the C–B and S(VI)–F bonds, including halogenation, Suzuki coupling, hydrogenation, and the SuFEX click reaction, which demonstrated the great potential of the VFSB moieties for use in skeleton linkage and drug modification.

Introduction

Click chemistry has become an essential tool in the fields of drug discovery, materials science, and bioconjugation due to its practicality, modularity, and ability to attach complex substances for chemoproteomic, pharmacological, and various biomimetic applications.[1–5] Extensive research has been conducted on sulfur(VI) fluoride exchange (SuFEx) chemistry as a next-generation click reaction[6] that relies on unique chemical properties, including hydrolytic stability, resistance to reduction, and chemoselective reactivity at the sulfur center.[7–18] The versatile bifunctional handles can be used as valuable linkers and key intermediates in organic synthesis and drug discovery.[19–21] However, the construction of bifunctional connectors containing the fluorosulfonyl group, which depends on multiple functional groups for subsequent derivatization, and allowing for the linkage and modification of different drug molecules, has rarely been reported[22,23] (Fig. 1A, bottom).

Recently, indirect methods have been developed for the rapid installation of single fluorosulfonyl groups in organic molecules, including the chloride–fluoride exchange of sulfonyl chlorides,[24–26] SO₂ insertion/fluorination,[27–30] electrophilic fluorination of thiols, and anodic oxidative fluorination.[31–34] Additionally, direct functionalizations to access monofunctional sulfonyl fluoride compounds have been realized through emerging fluorosulfonylating reagents[35–37] and sulfonyl fluoride building blocks[38–43] (Fig. 1A, upper arrow). However, the preparation of bifunctional fluorosulfonyl borides through the direct fluorosulfonyl-borylation of unsaturated hydrocarbons is greatly challenging and thus remains unexplored.

The vicinal fluorosulfonyl borides (VFSBs) are novel and practical bifunctional molecular connectors with great application potential because they can be readily converted to a myriad of diversified and valuable compounds through the transformation of the C–B bond and S(VI)–F bond via halogenation,[44] Suzuki coupling,[45–49] hydrogenation,[50] and elaboration of different drug molecules[51–55] (Fig. 1B, i). Thus, there is a robust demand for the development of efficient synthetic strategies for the stereo- and regioselective introduction of fluorosulfonyl and boronated functionalities into unsaturated hydrocarbons.

Typically, a radical borylation process often employs nucleophilic Lewis basic solvents/mediators for the activation of diboron reagents via homolytic cleavage of B–B bonds.[56–62] However, exogenous Lewis base-activated diboron species inevitably deplete highly active SO₂F reagents, and are unable to engage in the desired fluorosulfonyl-borylation sequence (Fig. 1B, ii). Several issues need to be addressed due to the complexity of the radical process incorporating C–S and C–B

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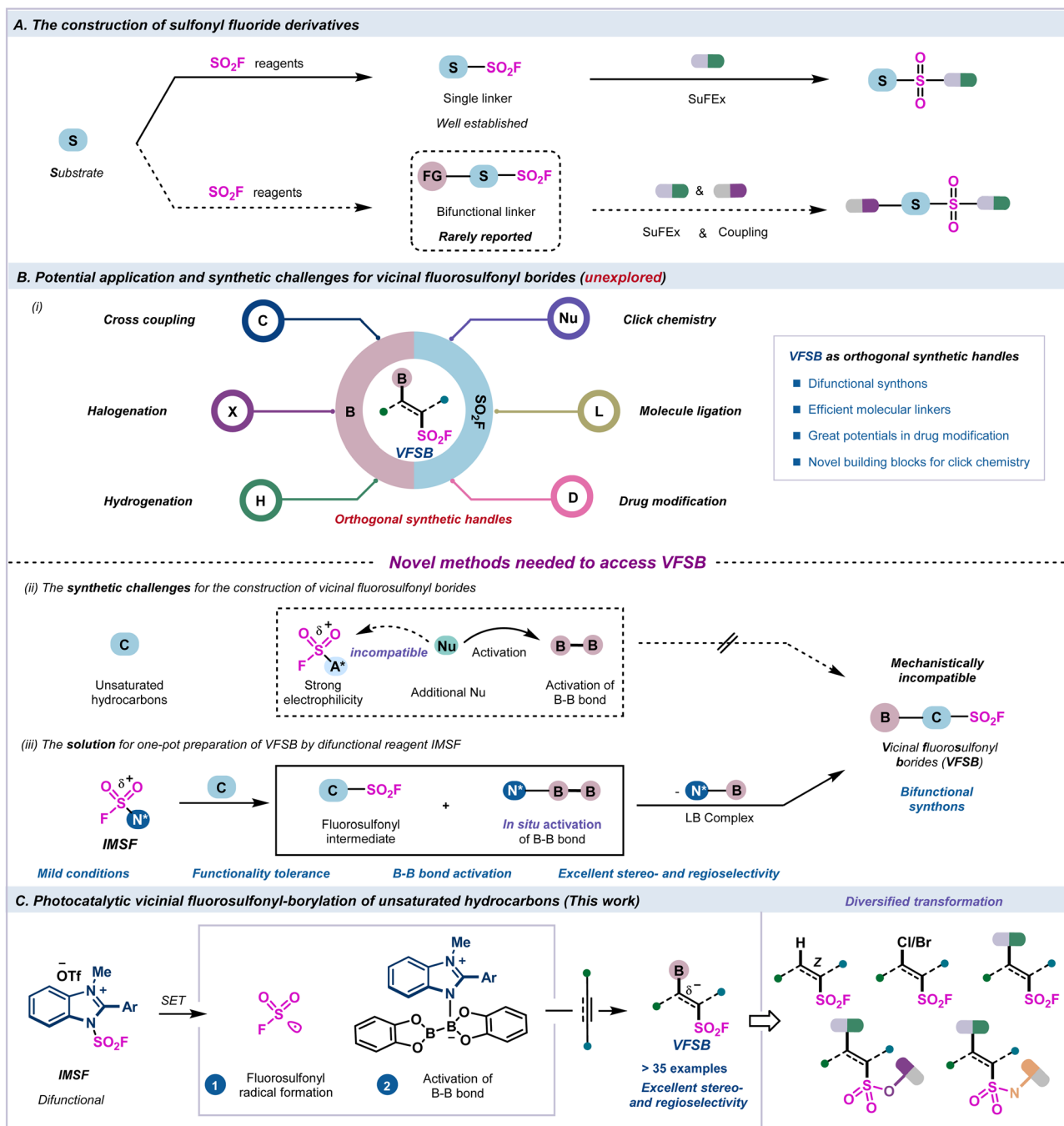
Fig. 1 Origin of the reaction design. (A) The construction of sulfonyl fluoride derivatives. (B) Potential application and synthetic challenges for vicinal fluorosulfonyl borides. (C) Photocatalytic vicinal fluorosulfonyl–borylation of unsaturated hydrocarbons.

bond formation, including the efficiency of B–B bond activation, the reactivities of sulfur- and boron-centered radicals, and the stereo- and regioselectivity of the radical additions to asymmetrical alkynes.

Recently, we developed an air-stable redox-active imidazolium fluorosulfonate (IMSF) reagent that was successfully employed for the stereoselective synthesis of alkenyl sulfonyl fluorides and functional alkyl sulfonyl fluorides.[35] Inspired by the *in situ* activation strategy of radical borylation,[44,63] we

envisioned that the bench-stable radical fluorosulfonylating reagent IMSF would be ideal for use as an integrated difunctional reagent for the fluorosulfonyl-borylation of unsaturated hydrocarbons. This highly active cationic salt underwent the SET process to generate the SO$_2$F radical. The endogenous imidazole residue subsequently activated the B–B bond for further borylation to realise the fluorosulfonyl-borylation process, and the use of an external Lewis base that may be detrimental to the SO$_2$F moiety is unnecessary (Fig. 1B, iii).

Herein, we successfully prepared a series of VFSB derivatives with excellent stereo- and regioselectivity through a photo-catalyzed radical fluorosulfonyl-borylation process (Fig. 1C).

Results and discussion

To showcase the protocol, we selected 3-cyclohexylpropyne (**1a**) as a pilot substrate to test the fluorosulfonyl-borylation (Table 1). After extensive efforts to identify the optimal conditions, we found that when using 2.5 equivalents of benzimidazolium sulfonate reagent (IMSF, **2a**), 2 mol% of 4CzIPN, and 2.5 equivalents of 2,2′-bis-1,3,2-benzodioxaborole (B$_2$Cat$_2$, **3**) in EtOAc (2 mL) under the irradiation of 60 W blue LEDs, fluo-rosulfonyl boride **4a** was obtained in 23% yield with >20 : 1 Z/E ratio. Because the catechol boronate product is not stable, the crude reaction mixture was converted to the corresponding 1,1,2,2-tetraethylethylene glycol borate ester (B(EPin)), which is more stable than pinacol borate on silica gel.[64]

Next, the various benzimidazolium sulfonate reagents were examined (Table 1). When cationic reagents **2b–2d** were used, the desired fluorosulfonyl boride **4a** was obtained in much lower yields, which may due to the relatively high negative reduction potential (entries 2–4). The yield of **4a** decreased when *fac*-Ir(ppy)$_3$ was used as the photocatalyst instead of 4CzIPN (entry 5). When the reaction proceeded with 90 W blue LEDs, the borylated product was afforded in 46% yield (entry 6).

This result indicated that the light intensity was critical to the fluorosulfonyl-borylation of unsaturated hydrocarbons.

Table 1 Optimization of the reaction conditions

Entry	Variation from the above condition	Yield[a]	$Z:E$[b]
1	None	23	>20 : 1
2	**2b** instead of **2a**	8	>20 : 1
3	**2c** instead of **2a**	9	>20 : 1
4	**2d** instead of **2a**	5	>20 : 1
5	*fac*-Ir(ppy)$_3$ instead of 4CzIPN	11	>20 : 1
6	90 W blue LEDs	46	>20 : 1
7	IA[c] (1 mL), 90 W blue LEDs	60	>20 : 1
8	**IA[c] (0.6 mL), 90 W blue LEDs**	**95 (70)[d]**	**>20 : 1**
9	w/o 4CzIPN	0	—
10	In the darkness	0	—

[a] Yield determined by gas chromography (GC) using dodecane as an internal standard. [b] The $Z:E$ ratio was determined by ^{1}H NMR and GC. [c] IA = Isopropyl acetate. [d] Isolated yield.

When isopropyl acetate (IA) was used as the solvent for the reaction, the yield of product **4a** was slightly increased (entry 7). The concentration of the reaction mixture was found to be significant for this transformation, as evidenced by the excellent yield (95% GC yield) obtained when the amount of solvent was decreased (entry 8). In addition, no product was detected in the absence of photocatalyst or light, demonstrating the essential role of all these components.
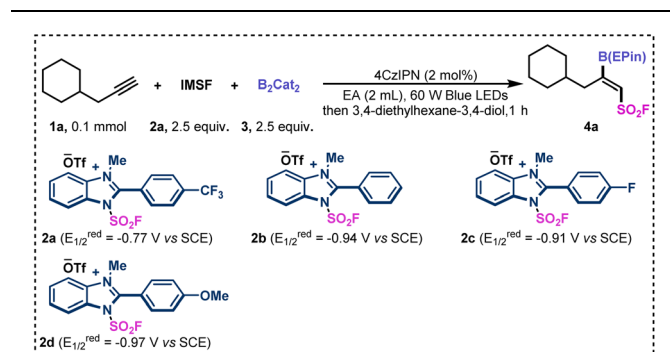
After we determined the optimized reaction conditions, we next examined the generality of this transformation with different alkynes (Scheme 1). First, we expanded the substrate scope for alkyl-substituted alkynes under standard conditions. Terminal alkynes bearing halides, aromatics, and aliphatics were able to uniformly furnish the target products (**4b–4e**) in moderate yields (52–62%) with high stereoselectivity. Subse-quently, we extended the substrate scope to various alkynes containing saturated carbocyclic structures. Strained cyclo-propyl- and cyclobutyl-derivatized substrates, especially fluori-nated cyclopropyl- and cyclobutyl-derivatized alkynes, provided the corresponding vicinal fluorosulfonyl borides (**4f–4h, 4j**) in moderate to satisfactory yields. The reaction can also be applied to saturated five-membered carbocycle-derivatized alkynes to afford (*Z*)-selective fluorosulfonyl boronate **4i** in 64% yield.

We also selected a number of alkynes containing natural drug molecules to test the fluorosulfonyl-borylation process. Glimepiride- and lumacator-derivatized terminal alkynes affor-ded fluorosulfonyl borylated products (**4k–4l**) in moderate yields with high stereoselectivity. We also extended this fluorosulfonyl-borylation protocol to a range of aryl alkynes. Aryl alkynes with electro-withdrawing or electro-donating substituents produced the desired products **4m–4v** in moderate to satisfactory yields with high stereo- and regiose-lectivity ($Z:E$ > 20 : 1). Naphthyl- and thienyl-substituted alkynes were also readily converted into the (*Z*)-fluorosulfonyl products **4w** and **4x** in moderate yields.

The adjacent fluorosulfonyl alkylborides are also useful bifunctional linkers in relevant fields of drug design and bio-conjugation. We applied this radical fluorosulfonyl-borylation protocol for the construction of vicinal fluorosulfonyl alkyl-borides. By slight variation of the standard conditions, we extended this radical fluorosulfonyl-borylation strategy to a series of unactivated alkenes (Scheme 2). The aryl-substituted butene derivatives afforded the target products **6a–6e** in moderate to satisfactory yields (62–86%). Additionally, 1-vinyl-cyclohexane, allylbenzene, and dodecene were compatible with the reaction system and generated the desired products (**6f, 6i–6j**) in moderate to satisfactory yields (39–81%). Alkenes bearing boronate were also tolerated and transformed into desired product **6k**. It is noteworthy that mono-substituted alkenes derived from liquid crystal building blocks, such as *trans, trans*-4-butyl-4′-vinylbicyclohexyl, and 4-*p*-tolyl-4′-vinyl-bi(cyclohexane), afforded β-fluorosulfonylborides (**6l** and **6m**) in moderate yields. In addition, terminal alkenes bearing ester functionality were also tolerated, and the desired product was smoothly obtained (**6n**).

To demonstrate the synthetic value of the VFSB moiety, derivatization of the fluorosulfonyl borides was carried out
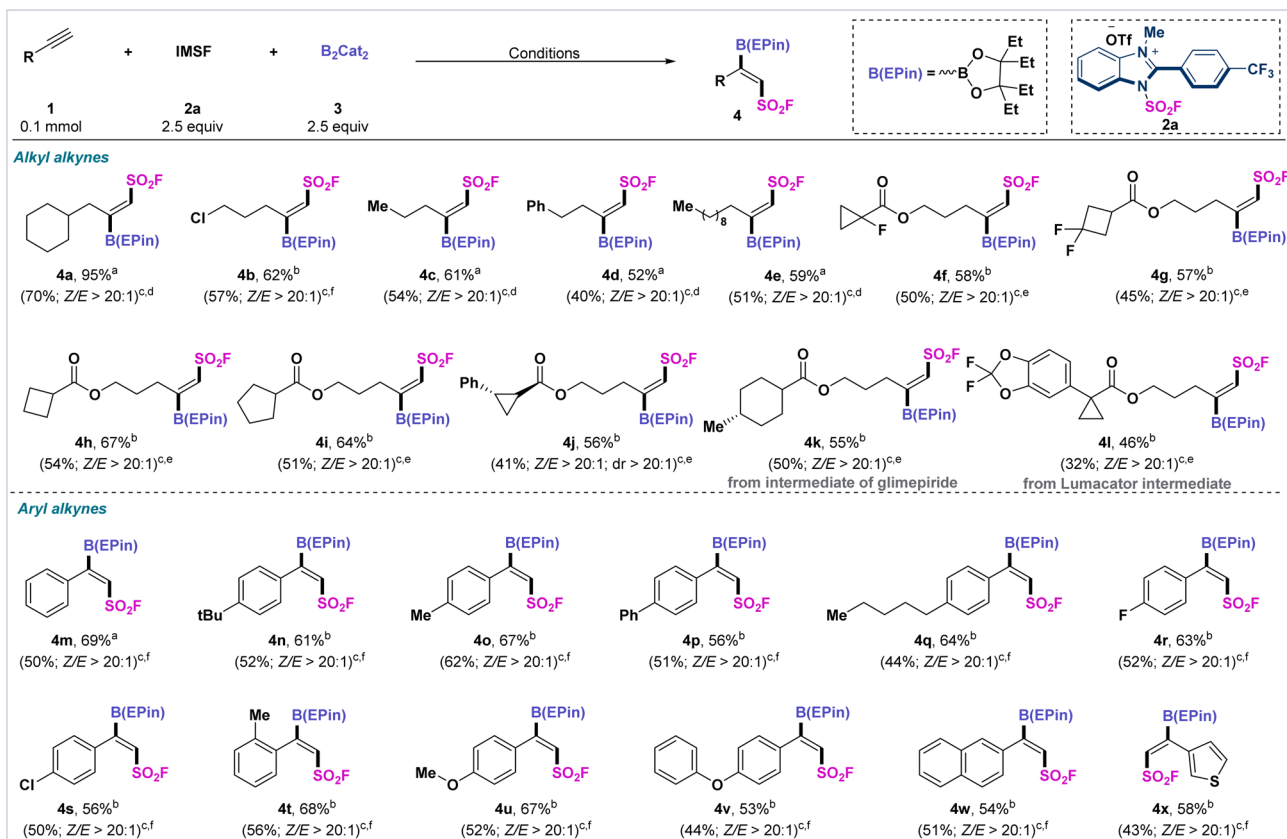
Scheme 1 Substrate scope of the alkynes. [a] Crude yields determined by GC using dodecane as an internal standard. [b] Crude yields determined by ^{19}F NMR spectroscopy using phenylmethylsulfonyl fluoride as an internal standard. [c] Values in parentheses are of isolated yields. [d] Condition A: all reactions were carried out with alkynes 1 (0.10 mmol), 2a (2.5 equiv.), B$_2$Cat$_2$ (3.0 equiv.), and 4CzIPN (2 mol%) in isopropyl acetate (0.6 mL) under Ar and 90 W blue LEDs for 40 min–12 h. Then, 3,4-diethyl-3,4-hexanediol was added to the reaction system, which was stirred for 1 h. [e] Condition B: isopropyl acetate: ethyl acetate = 2 : 1 (0.8 mL) was used. [f] Condition C: 13 h was used.
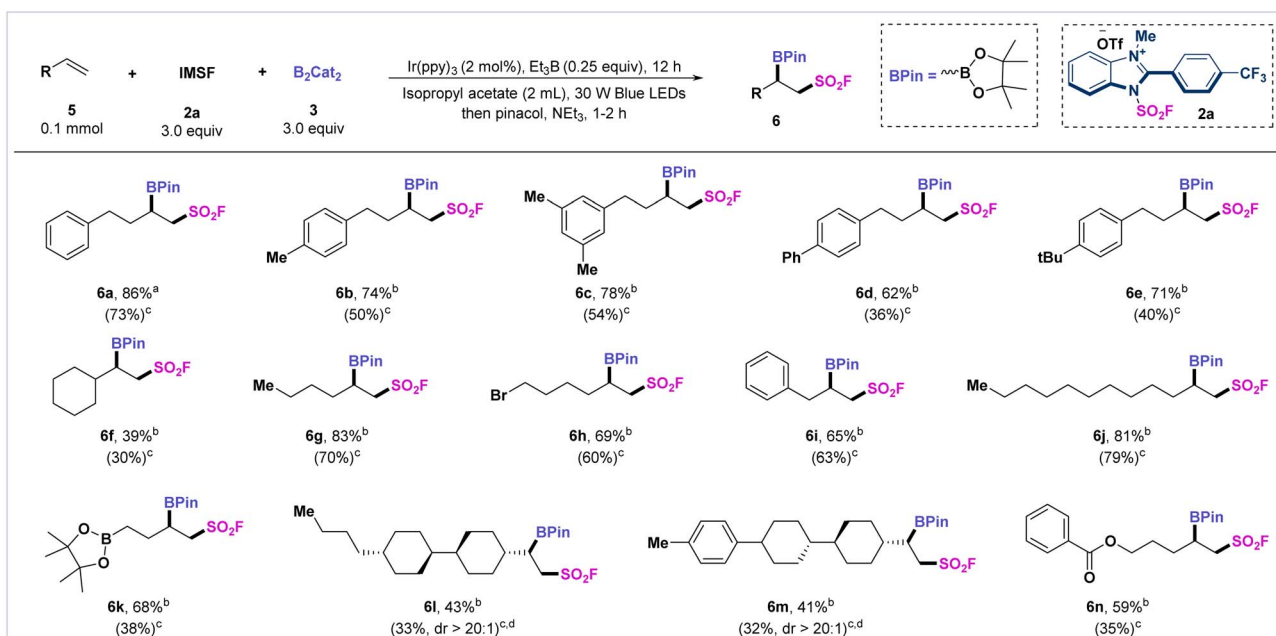
Scheme 2 Substrate scope of the olefins. [a] Crude yields determined by GC using dodecane as an internal standard. [b] Crude yields determined by ^{19}F NMR spectroscopy using phenylmethylsulfonyl fluoride as an internal standard. [c] Values in parentheses are of isolated yields. [d] The diastereomeric ratio was determined by ^{1}H NMR and ^{19}F NMR.
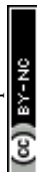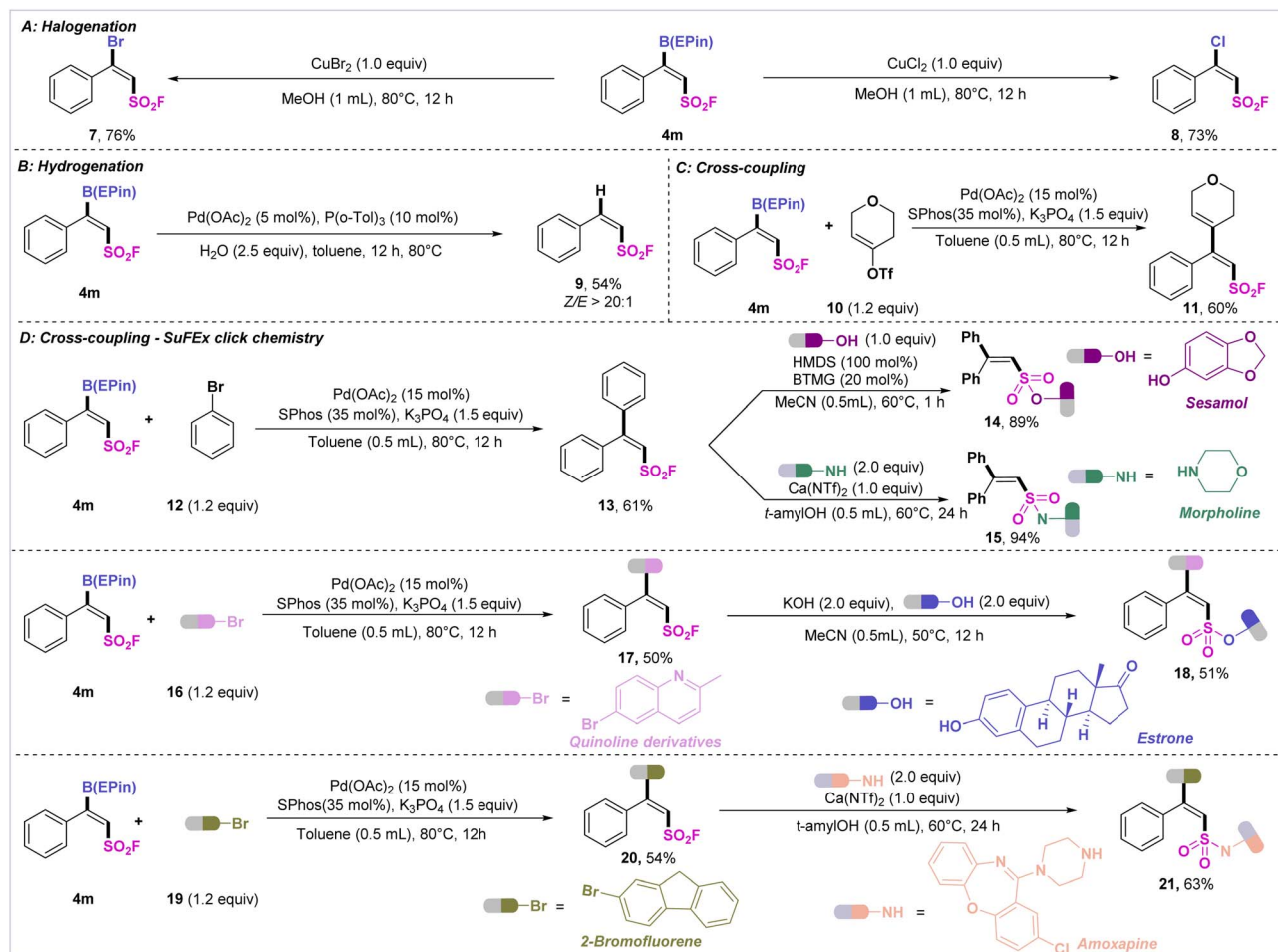
Scheme 3 Synthetic applications. (A) Halogenation of fluorosulfonyl boride **4m**. (B) Hydrogenation of borylated product **4m**. (C) Suzuki–Miyaura cross-coupling of **4m** with alkenyl sulfonate **10**. (D) Sequential Suzuki–Miyaura cross-coupling and SuFEx click reaction for drug molecule elaboration.

(Scheme 3). First, **4m** was treated with copper bromide or copper chloride to afford β-bromo alkenylsulfonyl fluoride **7** or β-chloro alkenylsulfonyl fluoride **8**. The palladium-catalyzed hydrogenation of **4m** furnished the desired product **9** with a high Z/E ratio (>20 : 1). Palladium-catalyzed Suzuki–Miyaura cross-coupling of **4m** with tetrahydro-4-pyrone-derived triflate **10** and bromobenzene **12** afforded the corresponding trisubstituted alkenes **11** (60%) and **13** (61%).

It is well known that sulfonyl fluoride species readily undergo various SuFEx reactions to connect other molecules. Thus, we tentatively attempted to ligate sulfonyl fluoride **13** with sesamol and morpholine, which afforded the desired sulfonated lipid product **14** and sulfonamide **15** in excellent yield. Finally, to verify the continuous functionalization of the VFSBs, **4m** was coupled with bromoquinoline and estrone to access the difunctionalized **18**. Also, the sequential linkage of **4m** with 2-bromofluorene and amoxapine furnished **21** in high efficiency.

To gain insight into this reaction, several mechanistic experiments were carried out (Scheme 4). First, the luminescence quenching experiment indicated that an excited state photocatalyst (PC*) can be quenched by **IMSF-2a**, which involved an oxidative quenching catalytic cycle (Scheme 4A).

Then, the ^{11}B NMR experiments indicated that only *in situ*-generated imidazole residue can activate the diboron reagent, as evidenced by the newly generated peak of 19.31 ppm (Scheme 4B; for details, see ESI Supplementary Fig. 10–13†). Finally, the radical trapping experiment using 3 equivalents of TEMPO resulted in inhibition of the radical addition. The addition of radical scavenger 1,1-diphenylethylene under the standard conditions yielded only trace amount of the product **4a**. The radical captive product **13** was isolated in 66% yield (Scheme 4C).

From the above mechanistic experiments, we speculate on the possible mechanism of the reaction in Scheme 4D. First, under irradiation, cationic reagent **2a** can be reduced by PC* to generate radical intermediate **I**, and it releases the SO₂F radical and imidazole residue **II**. Then, the addition of the SO₂F radical to the alkynes regioselectively furnishes vinylic radical intermediate **III**. Subsequent addition of vinyl radical **III** to B₂cat₂ afforded Z-vinyl diboron radical species **IV**. The control of stereoselectivity is governed by steric repulsion between the fluorosulfonyl group and the boronates.[44] Then, the activation of diboron reagent by *in situ*-generated imidazole residue **II** forms a highly reactive B–N heteroleptic intermediate **V**, which leads to the desired bifunctional products **4** or **6** and imidazole-
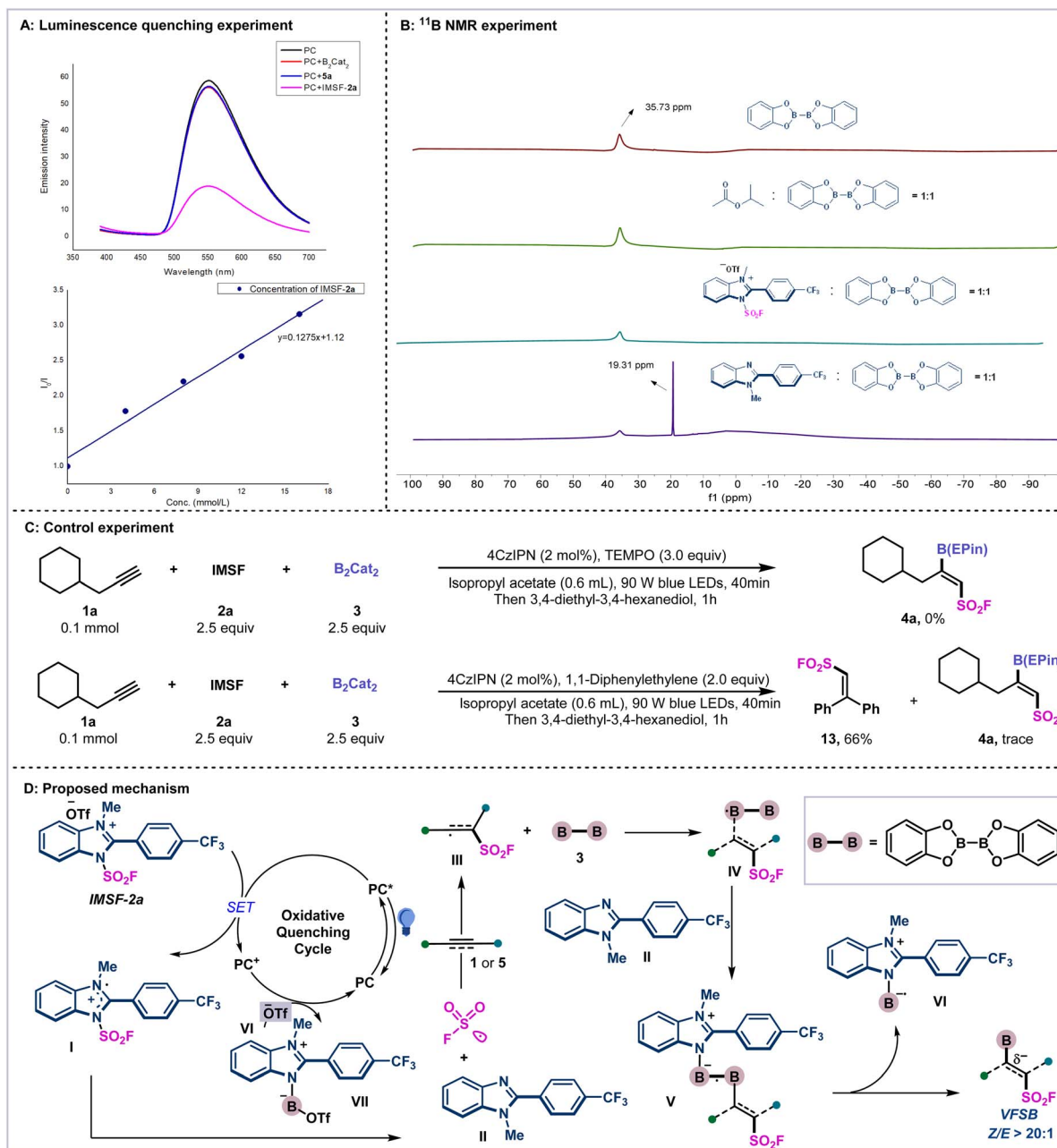
Scheme 4 Mechanistic studies and proposed mechanism. (A) Luminescence quenching experiment. (B) ^{11}B NMR experiments. (C) Control experiments. (D) Proposed mechanism.

stabilized boryl radical species **VI**. Finally, photo-oxidation of **VI** followed by coupling with $^-$OTf affords boryl imidazolium salt **VII** and regenerates PC.

Experimental

General procedure for the synthesis of products 4a and 4c–4e. Condition A

Under argon, corresponding alkynes **1a** and **1c–1e** (0.1 mmol) were added to a solution of 4CzIPN (2 mol%), 2,2′-bis-1,3,2-benzodioxaborole **3** (0.25 mmol, 2.5 equiv.), and IMSF reagent **2a** (0.2 mmol, 2.0 equiv.) in dried isopropyl acetate (0.6 mL) at

room temperature. The tube was then exposed to a 90 W blue LED for approximately 40 min–12 h, after which 3,4-diethyl-3,4-hexanediol was added to the reaction system, which was stirred for 1 h. The reaction was monitored by TLC analysis to determine completion, and the reaction mixture was evaporated in *vacuo*. The crude products were directly purified by flash chromatography on silica gel to yield the desired products.

General procedure for the synthesis of products 4b and 4f–4l. Condition B

Under argon, corresponding alkynes **1b** and **1f–1l** (0.1 mmol) were added to a solution of 4CzIPN (2 mol%), 2,2′-bis-1,3,2-

benzodioxaborole **3** (0.25 mmol, 2.5 equiv.), and IMSF reagent **2a** (0.2 mmol, 2.0 equiv.) in dried isopropyl acetate : ethyl acetate = 2 : 1 (0.8 mL) at room temperature. The tube was then exposed to a 90 W blue LED for approximately 40 min–12 h, after which 3,4-diethyl-3,4-hexanediol was added to the reaction system, which was stirred for 1 h. The reaction was monitored by TLC analysis for completion, and the reaction mixture was evaporated in *vacuo*. The crude products were directly purified by flash chromatography on silica gel to yield the desired products.

General procedure for the synthesis of products 4m–4x. Condition C

Under argon, corresponding alkynes **1m–1x** (0.1 mmol) were added to a solution of 4CzIPN (2 mol%), 2,2′-bis-1,3,2-benzodioxaborole **3** (0.25 mmol, 2.5 equiv.), and IMSF reagent **2a** (0.2 mmol, 2.0 equiv.) in dried isopropyl acetate (0.6 mL) at room temperature. The tube was then exposed to a 90 W blue LED for approximately 13 h, after which 3,4-diethyl-3,4-hexanediol was added to the reaction system, which was stirred for 1 h. The reaction was monitored by TLC analysis for completion, and the reaction mixture was evaporated in *vacuo*. The crude products were directly purified by flash chromatography on silica gel to yield the desired products.

General procedure for the synthesis of product 6

Under argon, corresponding olefin **5** (0.1 mmol) was added to a solution of *fac*-Ir(ppy)$_3$ (2 mol%), BEt$_3$ (0.025 mmol, 0.25 equiv.), 2,2′-bis-1,3,2-benzodioxaborole **3** (0.3 mmol, 3.0 equiv.), and IMSF reagent **2a** (0.3 mmol, 3.0 equiv.) in dried isopropyl acetate (2 mL) at room temperature. The tube was then exposed to a 30 W blue LED for approximately 12 h, after which pinacol and triethylamine was added to the reaction system, which was stirred for 1–2 h. The reaction was monitored by TLC analysis for completion, and the reaction mixture was evaporated in *vacuo*. The crude products were directly purified by flash chromatography on silica gel to yield the desired products.

Conclusion

The first fluorosulfonyl-borylation of unsaturated hydrocarbons using inexpensive and scalable benzimidazolium sulfonate as the difunctional reagent was successfully established under mild conditions. The highly active cationic reagent IMSF generated the SO$_2$F radical through the SET process and simultaneously *in situ*-generated imidazole residue to enable activation of the B–B bond. The vicinal fluorosulfonyl borides (VFSBs) are a combination of sulfonyl fluorides with boronates, and they provided a powerful bifunctional linker for selective assembly of different drug molecules. Based on the varieties of the VFSB scaffold, derivatizations of the borides and the sulfonyl fluorides can be readily realized, and they exhibit superior compatibility and extensive application of VFSB in the development of synthetic, bioconjugation, and medicinal tools.

Data availability

The data that support the findings of this study are available in the ESI† or upon request from the corresponding author.

Author contributions

H. L. conducted all experiments and characterized the novel compounds. Y. W., W. Z., and H. L. designed the experiments. W. Z., H. L., and Y. W. wrote the manuscript. Y. P. was responsible for the funding application. M. H., Z. Z., Z. W., Y. L., C. S., and W. C. contributed to the analysis and interpretation of the data.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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