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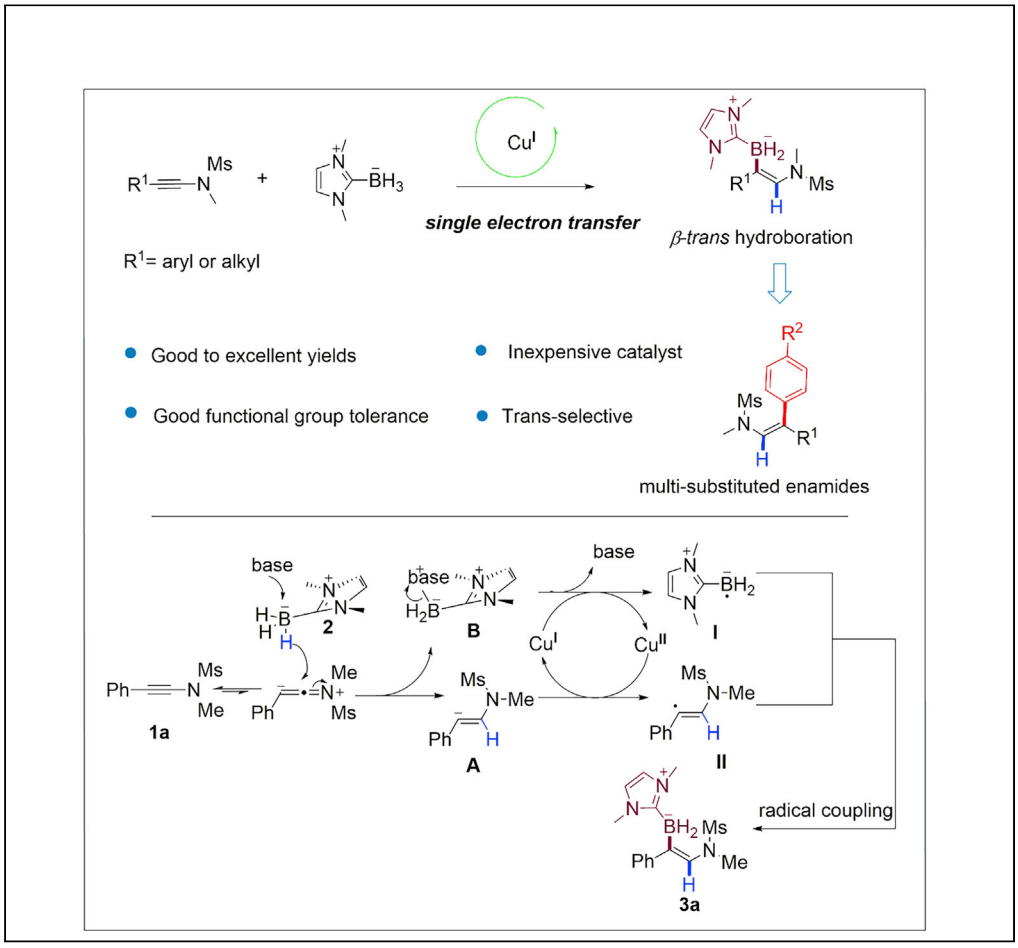

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Highlights

A Cu-catalyzed highly regio- and stereoselective radical *trans*-hydroboration of ynamides

Good to excellent yields, good functional group tolerance

Further investigation showcased that our method is robust and scalable

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Copper-catalyzed radical *trans*-selective hydroboration of ynamides with *N*-heterocyclic carbene boranes

Kefeng Wang,[1] Qingzhen Yu,[4] Wenli Mao,[1] Yuxin Zheng,[1] Jing Xu,[3,*] and Yukun Wang[1,2,5,*]

SUMMARY

Vinylboron compounds are important compounds in organic chemistry and biology. In this communication, we developed a copper(I)-catalyzed, highly regio- and stereoselective radical *trans*-hydroboration of ynamides with *N*-heterocyclic carbene (NHC)-ligated borane is reported, which leads to a series of *trans*-boryl enmides that can be conveniently transformed into various multi-substituted enamides. Further investigation showcased that our method is robust and scalable. The mechanism of this unique reaction is studied and discussed.

INTRODUCTION

Polysubstituted alkenes with versatile building blocks play an important role in the natural products, drug molecules, and the synthesis of materials (Figure 1) (Aziz et al., 2013; Tran and Minehan., 2012; Wu et al., 2019; Liu et al., 2021). Vinylboron compounds, as subgroups of alkenes, have also been vastly used in the synthesis of multi-substituted olefins, through Suzuki−Miyaura coupling, Hayashi−Miyaura conjugate addition, Chan−Lam coupling, Petasis reaction, and stereospecific C−C bond forming reactions (Ojha and Prabhu., 2016; Li et al., 2018). To synthesize vinylboron compounds, the hydroboration of alkynes is one of the most straightforward and effective methods (Brown, 1975; Pelter et al., 1988). Examples of regio- and stereoselective *trans*-hydroboration of alkynes are rare and often require specially designed catalysts or unusual reactants. Reason of these results is that direct hydroboration with trivalent boranes has the concerted nature and the *cis*-selective property of migratory insertion when transition metal is involved (Shimoi et al., 2018; Vaulter and Alcaraz., 2014).

Ynamides are special alkynes in which a nitrogen atom is attached to the carbon-carbon triple bond directly (Evano et al., 2010; DeKorver et al., 2010; Wang et al., 2014). Owing to their unique reactivity of ynamides, synthesis of ynamides has attracted extensive attention in recent years (Pan et al., 2016; Dodd and Cariou., 2018; Wang et al., 2020). Since hydroboration of ynamides can result into valuable, multi-substituted alkenes with two potential functionalization sites, several examples of hydroboration of the ynamides have been reported. Witulski and co-workers firstly reported that terminal ynamide reacts directly with catecholborane to form a β-*cis*-vinylborane with exclusive regio- and stereoselectivity (Scheme 1A) (Witulski et al., 2000). In 2001, the group of Hoffmann reported that zirconocene catalyzed β-selective *cis*-hydroboration of internal ynamides through migration insertion and transmetallization (Scheme 1B) (Hoffmann and Bruckner., 2001). In 2014, Zhu and his co-workers developed a Cu-catalyzed α-selective *cis*-hydroboration of ynamides with Xantphos as the ligand (Scheme 1C) (He et al., 2014). Interestingly, a similar copper(I) catalytic system composed of different phosphorus ligands catalyzed the hydroboration of internal ynamides could reverse the regioselectivity to yield an β-selective *cis*-adduct, as reported by Zhu in 2015 (Scheme 1D) (Bai et al., 2015). Despite the well-developed methods of the *cis*-hydroboration of ynamides, the *trans*-hydroboration of ynamides is rarely reported. Especially, a copper-catalyzed *trans*-hydroboration has not been reported.

Different from the above typical concerted hydroboration and organometallic hydroboration mechanism, in 2019, Wang and co-workers reported an Et_2Zn-initiated radical *trans*-hydroboration of ynamides with moderate yields using *N*-heterocyclic carbene (NHC) boranes (Scheme 1E) (Wang et al., 2020). In their report, the usage of pyrophoric Et_2Zn leaves spaces for improvement. Copper is a cheap and abundant metal element in the earth, and a kind of low-toxicity metal. Moreover, copper has good single electron transfer properties, which has been widely used in the field of free-radical chemistry in recent years

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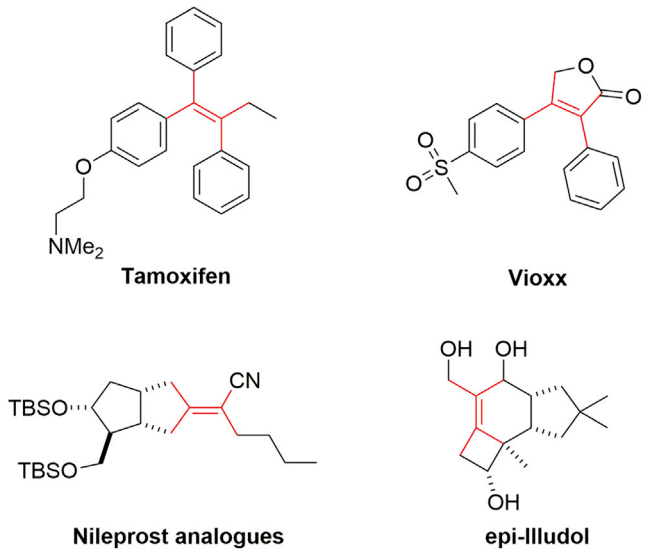


Figure 1. Biologically active polysubstituted alkenes

(Li et al., 2020). In this work, we used inexpensive and readily accessible copper salts as catalysts that promoted the radical *trans*-selective hydroboration of ynamides.

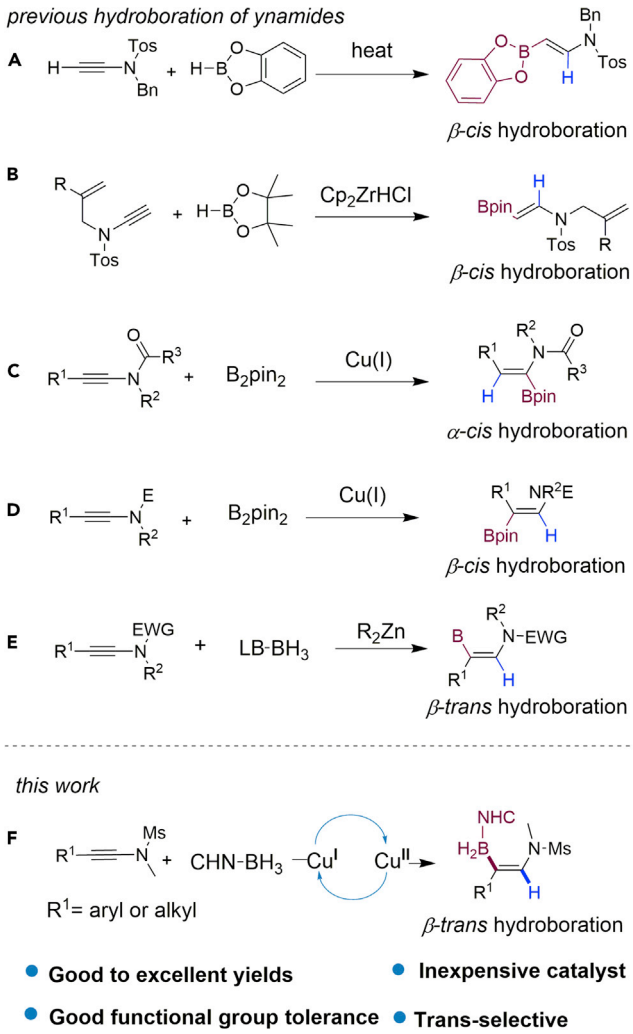
RESULTS AND DISCUSSION

Optimization of reaction conditions

Our preliminary studies used phenyl-substituted *N*-sulfonyl ynamide **1a** with 1,3-dimethylimidazol-2-ylidene borane **2** as model systems. In the initial experiments, the CuCl/*t*-BuOK-catalyzed hydroboration of **1a** and **2** at 70°C with phosphine ligands (Lee et al., 2008; Yoshida et al., 2012) did not produce any detectable amount of the desired product **3a** (Table 1, entries 1–2). In addition, when the hydroboration of **1a** and **2** was catalyzed by NHC-CuCl/*t*-BuOK system (Park et al., 2012), the desired product **3a** was not obtained either (entry 3). These results indicated that the electronic effect of ligands or the steric hindrance is not conducive to the formation of the target product. To our pleasure, the CuCl-catalyzed hydroboration of **1a** with **2** afforded the *trans*-hydroboration product **3a** as a single regio- and stereoisomer (Wang et al., 2020), which was given in 37% yield (entry 4). Encouraged by this result, the other copper salt catalysts, such as $CuCl_2$, $Cu(OTf)_2$ and $Cu(OAc)_2$. However, no one exhibited good catalytic reactivity under otherwise identical conditions (entry 5–7). Among the bases examined, *t*-BuOK showed the highest reactivity in these reactions (entry 8–10). Solvent effect plays a substantial role in this reaction, and chlorobenzene gave the highest yield (entry 11–18). It was also observed that CuCl is essential to this transformation. No reaction occurred when only *t*-BuOK was used. Higher base loading (20 mol %, 50 mol % or 1 equiv) resulted in lower yields. Lower temperatures resulted in prolonged reaction time and lower yields, while attempts to shorten the reaction time by elevating the reaction temperature (80°C or 100°C) also led to lower yields. Thus, the optimized reaction conditions were identified as: 20 mol % CuCl, 5 mol % *t*-BuOK, 3 equiv of NHC-BH_3, and 0.4 M in chlorobenzene at 70°C for 40 h (entry 11).

Substrate scope

With the optimized condition in hand (Table 1, entry 11), we then examined the hydroboration of ynamides with various substituted phenyl groups, as shown in Scheme 2. The reactions of *N*-sulfonyl-arylynamides with various electron withdrawing groups (EWGs, **3b–j**) and electron donating groups (EDGs, **3L–n**) on the phenyl ring, all delivered the desired products in yields ranging from 70% to 82%. Substitutions at the para, meta, and ortho positions of aryl ynamides seem to barely have impact on their reactivity (**3b–3h**). Notably, the nitrile group was compatible well in this reaction (**3k**). A thiophen-substituted substrate was also suitable for hydroboration (**3q**). Equally important is that alkyl ynamides also gave satisfactory results (**3r–3u**).



Scheme 1. Hydroboration of ynamides

(A and B) Hydroboration terminal ynamides.

(C and D) Cu-catalyzed *cis*-hydroboration of ynamides.

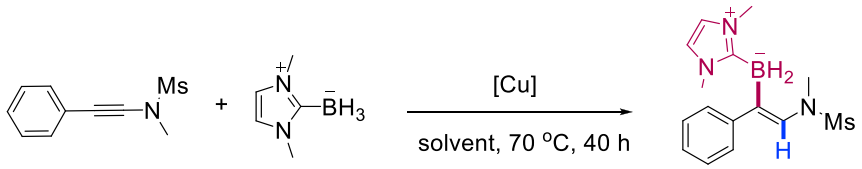
(E) $ZnEt_2$-promoted *trans*-hydroboration of ynamides.

(F) Cu-catalyzed radical *trans*-selective hydroboration of ynamides.

Mechanistic studies

We also investigated the reaction mechanisms of this intriguing transformation. First, when the deuterated NHC-BD_3 was used, fully deuterated hydroboration product was yielded (Scheme 3A). When the same equivalent of H_2O with NHC-BD_3 was added to the reaction, it also led to the deuterated hydroboration product (Scheme 3B). In contrast, adding the same equivalent of deuterium water with non-deuterated NHC-BH_3 to the reaction, the non-deuterated hydroboration product was observed (Scheme 3C). These experimental results clearly indicated that the hydrogen in the *trans*-hydroboration products comes from NHC-boranes. It is also evidenced that in the side hydrogenation products, the α-hydrogen comes from the NHC-BH_3 as well, while the β-hydrogen comes from H_2O in the reaction mixture (Schemes 3A and 3B). Under standard conditions, the equivalent addition of H_2O led to complete conversion of the hydroboration product to the side hydrogenation product (Scheme 3D), which suggest that the side product was hydrolyzed from the hydroboration product. Competition experiments with equal amount of NHC-BH_3 and NHC-BD_3 revealed a primary isotope effect value of 2.3, which excludes a concerted reaction mechanism (Scheme 3E). Radical trapping experiments with TEMPO drastically lowered the yield of hydroboration product (22%), and the TEMPO adduct was isolated in 27% yield (Scheme 3F), which clearly indicating the free radical pathway.

Table 1. Optimization of the reaction conditions[a]



1a **2** **3a**

Entry	Cu (20 mol %)	Ligand (10mol %)	Base (5mol %)	Solvent (0.4M)	Yield (%)[b]
1	CuCl	Xantphos	*t*-BuOK	toluene	0
2	CuCl	PCy_3	*t*-BuOK	toluene	0
3	NHC-CuCl	_	*t*-BuOK	toluene	0
4	CuCl	_	_	toluene	37%
5	$CuCl_2$	_	_	toluene	Trace
6	$Cu(OTf)_2$	_	_	toluene	Trace
7	$Cu(OAc)_2$	_	_	toluene	Trace
8	CuCl	_	*t*-BuOK	toluene	55%
9	CuCl	_	K_2CO_3	toluene	48%
10	CuCl	_	NaOAc	toluene	39%
11	**CuCl**	_	***t*-BuOK**	**PhCl**	**75%**
12	CuCl	_	*t*-BuOK	THF	47%
13	CuCl	_	*t*-BuOK	MeCN	45%
14	CuCl	_	*t*-BuOK	n-hexane	31%
15	CuCl	_	*t*-BuOK	TBA	43%
16	CuCl	_	*t*-BuOK	DCE	56%
17	CuCl	_	*t*-BuOK	DMF	Trace
18	CuCl	_	*t*-BuOK	DMSO	Trace

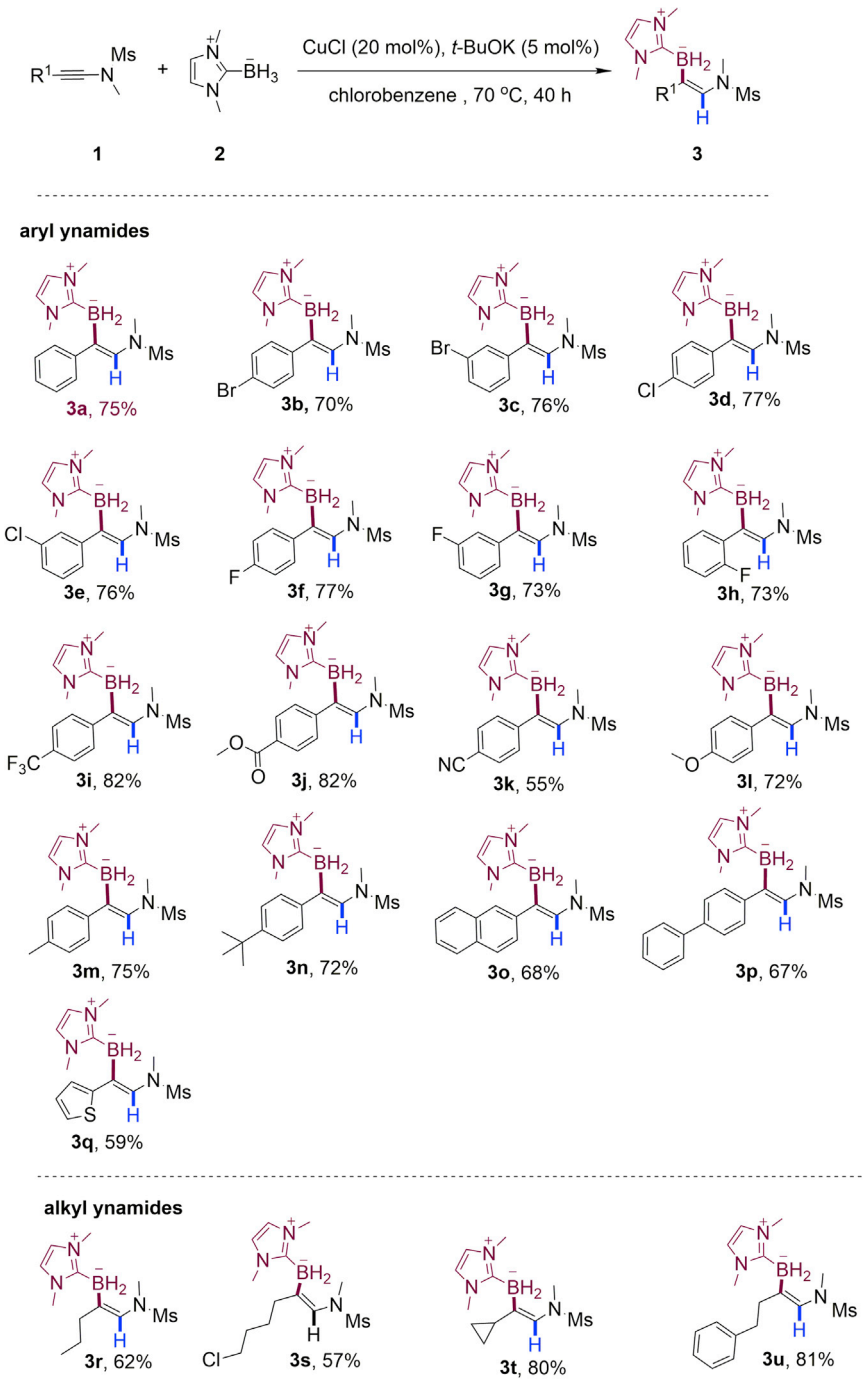
[a]Reaction conditions: **1a** (0.2 mmol), **2** (3.0 equiv), chlorobenzene (0.5 mL), Ar, 40 h.
[b]Isolated yields.

Plausible mechanism

On the basis of the results obtained and previous reports (Che et al., 2016; Ke et al., 2015), the plausible reaction mechanism is proposed in Scheme 4. Owing to the electron-donation effect of the nitrogen atom, the polarization of the ynamide triple bond generates a keteniminium resonance structure, which makes the α-carbon of the ynamide electrophilic. Hence, the hydride transfer from the NHC-BH_3 is expected to undergo in a regioselective manner. A borenium ion and a vinyl anion were released during this process, as similar species has been previously proposed (Wang et al., 2020; De Vries et al., 2012; McGough et al., 2016). Subsequently, the borenium ion is reduced to boryl radical **I** by Cu(I). On the other hand, the vinyl anion **A** was oxidized by Cu(II) to produce vinyl radical **II**, which has also been observed in the radical trapping experiment. Finally, boryl radical specie **I** and carbon radical specie **II** underwent a coupling reaction to produce the final product **3a**. In Scheme 2, compound **3t** was synthesized smoothly with a high yield which contains a cyclopropyl moiety. However, no ring-opening products were observed and isolated, which may contribute to the free radical addition reaction of the central carbon atom on the allene to obtain the ring compound under standard conditions (Crandall and Ayers., 1991; Apparu and Crandall., 1984).

Gram-scale synthesis and transformations of borylated products

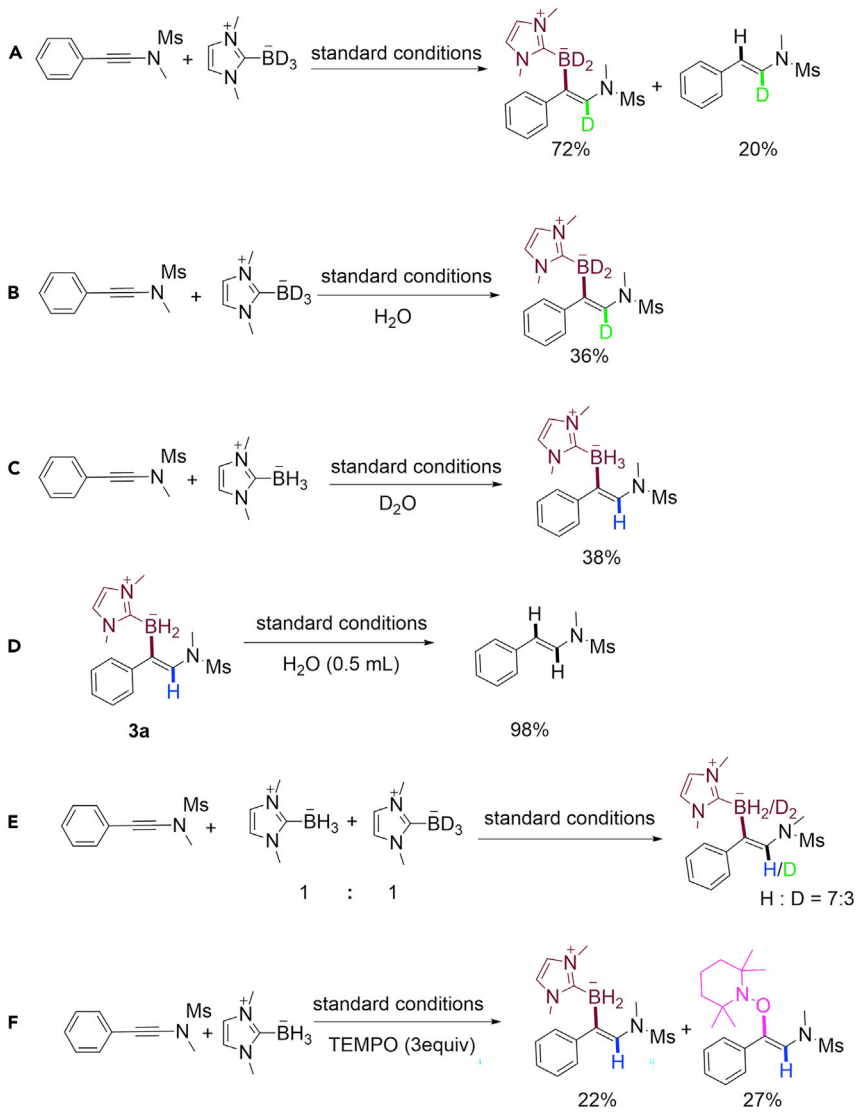
Furthermore, the potential synthetic utility was demonstrated by a gram-scale synthesis and the subsequent transformations of the borylated products. Phenyl-substituted *N*-sulfonyl ynamide **1a** was reacted with 1,3-dimethylimidazol-2-ylidene borane **2** under the standard reaction conditions with a slightly prolonged reaction time (48 h, Scheme 5A) to obtain 1.09 g of **3a** (68% yield). In the presence of $Pd(PPh_3)_4$



Scheme 2. Substrates scope of ynamides

Reaction conditions: **1** (0.2 mmol), **2** (3.0 equiv), CuCl (20 mol %), *t*-BuOK (5 mol %), chlorobenzene (0.5 mL), Ar, 70°C, 40 h. Isolated yield was given.

(10 mol %) and K_2CO_3 (5 equiv), **3a** was coupled with aryl iodides to furnish β,β-disubstituted alkenylamide **5a** and **5b** in 54% and 50% yields, respectively. Thus, our method also provides a simple, regio- and stereoselective route to fully substituted sulfonyl enamides (Schemes 5B and 5C).



Scheme 3. Mechanistic studies

(A–C) Deuteration experiments.

(D) Hydrolysis experiments.

(E) Intermolecular kinetic isotope effects.

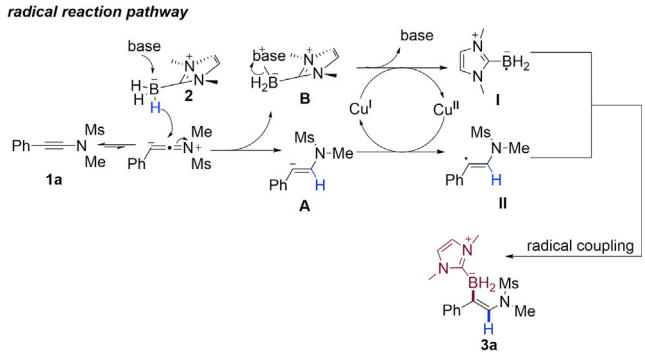
(F) Radical scavenger experiments.

Conclusion

In summary, a Cu-catalyzed radical *trans*-selective hydroboration of ynamides using NHC-boranes was developed. This reaction is compatible with a series of aryl and alkyl substituents and produces borylated enamides in moderate to good yields. The synthetic usefulness of this approach is well demonstrated by the following Suzuki-Miyaura coupling of resulting hydroboration products, which offers a regio- and stereoselective approach for the synthesis of various β,β-disubstituted sulfonyl enamides, an important and valuable synthetic building blocks in organic synthesis. The further investigations on the reaction mechanism and application to various bioactive enamides are currently undergoing in our laboratory.

Limitations of the study

The synthesis of *trans*-hydroboration products through this methodology remains a challenge, e.g. the substrate with Ts or Ns does not react completely under standard conditions. In addition, this reaction is



Scheme 4. A plausible mechanism

not compatible with 3-(2-phenylethynyl)oxazolidin-2-one. The further investigations on the reaction mechanism and application to various bioactive enamides still need to done.

STAR★METHODS

Detailed methods are provided in the online version of this paper and include the following:

- KEY RESOURCES TABLE
- RESOURCE AVAILABILITY
  - Lead contact
  - Materials availability
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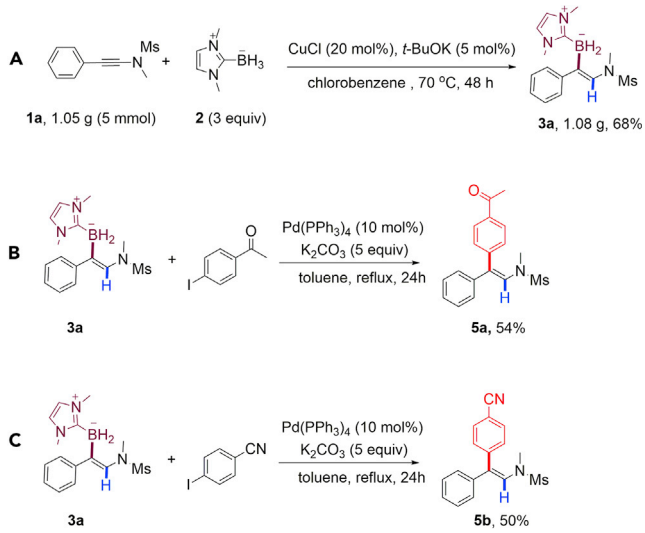
- METHOD DETAILS
  - Preparation of ynamides (for ynamides used in this work)
  - Preparation of boranes (for boranes used in this work)
  - General procedure for the synthesis of products
  - Spectroscopic details

SUPPLEMENTAL INFORMATION

Supplemental information can be found online at https://doi.org/10.1016/j.isci.2022.104977.



Scheme 5. Gram-scale synthesis and transformation of products

(A) Gram-scale synthesis.

(B and C) Product transformations.

ACKNOWLEDGMENTS

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AUTHOR CONTRIBUTIONS

J.X. and Y.-K.W. designed and supervised the project. K.-F.W. designed and performed the experiments; K.-F.W., Q.-Z.Y., W.-L.M., and Y.-X.Z. analyzed all the results. J.X. and Y.-K.W. prepared the paper. All the authors discussed the results and commented on the paper.

DECLARATION OF INTERESTS

The authors declare no competing interests.

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STAR★METHODS

KEY RESOURCES TABLE

REAGENT or RESOURCE	SOURCE	IDENTIFIER
Chemicals, peptides, and recombinant proteins		
Phenylacetylene	Energy Chemical	CAS:536-74-3
1-Bromo-4-ethynylbenzene	Energy Chemical	CAS:766-96-1
3-Bromophenylacetylene	Energy Chemical	CAS:766-81-4
4-Chlorophenylacetylene	Macklin	CAS:873-73-4
3-Chloro-1-ethynylbenzene	Alfa Aesar	CAS:766-83-6
4-Fluorophenylacetylene	Energy Chemical	CAS:766-98-3
1-Ethynyl-3-fluorobenzene	Energy Chemical	CAS:2561-17-3
2-Fluorophenylacetylene	Alfa Aesar	CAS:766-49-4
4-Ethynyl-α,α,α-trifluorotoluene	Macklin	CAS:705-31-7
4-Ethynylbenzoic acid methyl ester	Aladdin	CAS:3034-86-4
4-Ethynylbenzonitrile	Energy Chemical	CAS:3032-92-6
4-Ethynyl-1,1′-biphenyl	Energy Chemical	CAS:29,079-00-3
2-Ethynylnaphthalene	Energy Chemical	CAS:2949-26-0
4-Ethynylanisole	Macklin	CAS:768-60-5
4-Ethynyltoluene	Macklin	CAS:766-97-2
4-*tert*-Butylphenylacetylene	J&K Scientific	CAS:772-38-3
3-Ethynylthiophene	J&K Scientific	CAS:67237-53-0
4-Phenyl-1-butyne	J&K Scientific	CAS:16520-62-0
Cyclopropyl acetylene	J&K Scientific	CAS:6746-94-7
1-Pentyne	Alfa Aesar	CAS:627-19-0
6-Chloro-1-hexyne	TCI	CAS:10297-06-0
N-Bromosuccinimide	Aladdin	CAS:128-08-5
Copper sulfate pentahydrate	Sigma-Aldrich	CAS:7758-99-8
N-methyl methanesulfonamide	Aladdin	CAS:1184-85-6
Cupric chloride	Macklin	CAS:7447-39-4
Copper(I) chloride	Energy Chemical	CAS:7758-89-6
Pyridine	Macklin	CAS:110-86-1
Potassium carbonate	Aladdin	CAS:584-08-7
Sodium carbonate	Energy Chemical	CAS:497-19-8
1,3-Dimethylimidazolium iodide	Alfa Aesar	CAS:4333-62-4
4-Iodobenzonitrile	Aladdin	CAS:3058-39-7
4′-Iodoacetophenone	Aladdin	CAS:13329-40-3
Tetrakis(triphenylphosphine)palladium	Macklin	CAS:14221-01-3
Potassium tert-butoxide	Energy Chemical	CAS:865-47-4
2,2,6,6-Tetramethylpiperidinooxy	Energy Chemical	CAS:2564-83-2

RESOURCE AVAILABILITY

Lead contact

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Materials availability

All materials generated in this study are available within the article and the supplemental information or from the lead contact upon reasonable request.

Data and code availability

- All data reported in this paper will be shared by the lead contact upon request.
- This paper does not report original code.
- Any additional information required to reanalyze the data reported in this paper is available from the lead contact upon request.

METHOD DETAILS

All the fine chemicals were procured from Energy Chemical, Sigma-Aldrich, Aladdin, J&K Scientific, Alfa Aesar, Macklin or TCI chemicals and used directly. Thin-layer chromatography (TLC) of 0.25 mm silica gel aluminum plates (60F-254) was used to monitor the progress of the reaction, and visualization was done using UV light (254 or 365 nm). Visualization was accomplished with short wave UV light, or KMnO4、Phosphomolybdic Acid staining solutions followed by heating. Flash column chromatography was performed using silica gel (200-300 mesh) with solvents distilled prior to use. Proton (^{1}H), Carbon (^{13}C), Boron(^{11}B) and Fluorine NMR (^{19}F) were recorded at 400, 101, 128 and 376 MHz NMR spectrometer, respectively.

Preparation of ynamides (for ynamides used in this work)

To a solution of substituted phenylacetylenes (10.0 mmol) in acetone (30 mL) was added NBS (12.0 mmol) and $AgNO_3$ (169.9 mg, 1.0 mmol), the resulting mixture was stirred under Ar at room temperature for 2 h. After removing excess acetone, the reaction was quenched with saturated NH_4Cl solution. The organic layer was extracted with petroleum ether (20 mL x 2), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to afford bromoalkynes. To a dried flask was added *N*-methymethanesulphonamide (1.2 equiv), $CuSO_4 \cdot 5H_2O$ (0.1 equiv), 1,10-phenanthroline (0.2 equiv) and K_2CO_3 (2.5 equiv). The resulting mixture was subsequently treated with anhydrous toluene and bromoalkynes, and stirred at 80°C for overnight under Ar. After completion, the crude mixture was cooled to room temperature, filtered through celite, and concentrated in vacuo. The resulting residue was purified by flash column chromatography on silica gel, giving the pure ynamides. (Mukherjee et al., 2011; Karad et al., 2012).

$CuCl_2$ (0.2equiv), *N*-methylmethanesulfonamide (2.5 equiv) and Na_2CO_3 (2.0 equiv) were added to a flame-dried 50 mL three-necked round-bottomed flask. The flask was purged with oxygen for 15 min and a solution of pyridine (2.0 equiv) in dry toluene (0.2 M) was added. A balloon filled with oxygen was connected to the flask and the stirred mixture was heated at 70°C. After 15 min, a solution of alkyne (10.0 mmol, 1 equiv) in dry toluene (0.2 M) was added dropwise. The mixture was allowed to stir at 70°C for another 12 h and was then cooled to rt. The reaction mixture was concentrated under reduced pressure and the residue was purified by flash chromatography. (Hamada et al., 2008).

Preparation of boranes (for boranes used in this work)

Sodium borohydride (1.2 equiv) was added to a round-bottom flask containing imidazolium salt (1.0 equiv) and toluene (1 mL/mmol imidazolium). The flask was fitted with a cold water condenser and placed in an oil bath at 125–130°C for 18–24 h. The hot reaction solvent was cautiously decanted from the insoluble mixture, and the remaining residue was extracted with hot toluene (2 × 1 reaction volume). The combined organic extracts were concentrated under reduced pressure. The crude material was purified following the corresponding procedure. (Gardner et al., 2015).

General procedure for the synthesis of products

A mixture of Acetylene amine (0.2 mmol), NHC-borane (0.6 mmol), CuCl (20 mol %), *t*-BuOK (5 mol %) in dry chlorobenzene (0.5 mL) was stirred under Ar at 70°C for 40 h. After completion, the crude mixture was cooled to room temperature, filtered through celite, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel using petroleum ether/EtOAc as eluant.

Synthesis of (Z)-N-(2-(4-acetylphenyl)-2-phenylvinyl)-N-methylmethanesulfonamide

The reaction of $Pd(PPh_3)_4$ (0.01 mmol), K_2CO_3 (0.5 mmol) and **3a** (0.1 mmol), 1-(4-iodophenyl)ethan-1-one (0.15 mmol) in toluene (0.5 mL) reflux for 24 h afforded **5a** (17.7 mg, yield: 54%) as a yellow solid. (Zhu et al., 2014).

Synthesis of (Z)-N-(2-(4-cyanophenyl)-2-phenylvinyl)-N-methylmethanesulfonamide

The reaction of $Pd(PPh_3)_4$ (0.01 mmol), K_2CO_3 (0.5 mmol) and **3a** (0.1 mmol), 4-iodobenzonitrile (0.15 mmol) in toluene (0.5 mL) reflux for 24 h afforded **5b** (17.7 mg, yield: 50%) as a yellow solid. (Zhu et al., 2014).

Spectroscopic details

(*E*)-(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)(2-(*N*-methylmethylsulfonamido)-1-phenylvinyl)dihydroborate, **3a**: ^{1}H NMR (400 MHz, Chloro-form-*d*) δ 7.28 (dd, *J* = 8.2, 1.3 Hz, 2H), 7.21 (t, *J* = 7.4 Hz, 2H), 7.15–7.10 (m, 1H), 6.75 (s, 2H), 6.02 (s, 1H), 3.67 (s, 6H), 2.99 (s, 3H), 2.79 (s, 3H). ^{13}C NMR (101 MHz, Chloro-form-*d*) δ 148.28, 128.07, 127.70, 127.01, 125.54, 120.24, 37.97, 36.05, 33.71. ^{11}B NMR (128 MHz, Chloro-form-*d*) δ −28.18 (t, *J* = 86.7 Hz).

(*E*)-(1-(4-bromophenyl)-2-(*N*-methylmethylsulfonamido)vinyl)(1,3-dimethyl-1H-imidazol-3-ium-2-yl)dihydroborate, **3b**: ^{1}H NMR (400 MHz, Chloro-form-*d*) δ 7.32 (d, *J* = 8.4 Hz, 2H), 7.18–7.15 (m, 2H), 6.76 (s, 2H), 5.99 (s, 1H), 3.66 (s, 6H), 2.96 (s, 3H), 2.78 (s, 3H). ^{13}C NMR (101 MHz, Chloro-form-*d*) δ 147.24, 130.68, 128.75, 128.24, 120.33, 119.29, 37.87, 36.02, 33.73. ^{11}B NMR (128 MHz, Chloro-form-*d*) δ −28.28 (t, *J* = 86.7 Hz).

(*E*)-(1-(3-bromophenyl)-2-(N-methylmethylsulfonamido)vinyl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate, **3c**: ^{1}H NMR (400 MHz, Chloro-form-*d*) δ 7.37 (t, *J* = 1.9 Hz, 1H), 7.21–7.16 (m, 2H), 7.03 (t, *J* = 7.8 Hz, 1H), 6.72 (s, 2H), 5.97 (s, 1H), 3.63 (s, 6H), 2.93 (s, 3H), 2.75 (s, 3H). ^{13}C NMR (101 MHz, Chloro-form-*d*) δ 150.62, 129.91, 129.29, 128.74, 128.42, 125.72, 121.87, 120.37, 37.96, 36.08, 33.77. ^{11}B NMR (128 MHz, Chloro-form-*d*) δ −27.92 (d, *J* = 87.0 Hz), −28.93. HRMS (ESI-TOF): *m/z* calculated for $C_{15}H_{21}BBrN_3O_2S$ $[M + Na]^+$: 420.0526, found: 420.0534.

(*E*)-(1-(4-chlorophenyl)-2-(*N*-methylmethylsulfonamido)vinyl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate, **3d**ays: ^{1}H NMR (400 MHz, Chloro-form-*d*) δ 7.24–7.21 (m, 2H), 7.19–7.15 (m, 2H), 6.76 (s, 2H), 6.00 (s, 1H), 3.66 (s, 6H), 2.96 (s, 3H), 2.78 (s, 3H). ^{13}C NMR (101 MHz, Chloro-form-*d*) δ 146.75, 131.19, 128.34, 128.27, 127.75, 120.33, 37.89, 36.03, 33.71. ^{11}B NMR (128 MHz, Chloro-form-*d*) δ −28.27 (t, *J* = 86.5 Hz). HRMS (ESI-TOF): *m/z* calculated for $C_{15}H_{21}BClN_3O_2S$ $[M + Na]^+$: 376.1018, found: 376.1022.

(*E*)-(1-(3-chlorophenyl)-2-(*N*-methylmethylsulfonamido)vinyl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate, **3e**: ^{1}H NMR (400 MHz, Chloro-form-*d*) δ 7.27 (t, *J* = 1.8 Hz, 1H), 7.20–7.08 (m, 4H), 6.77 (s, 2H), 6.03 (s, 1H), 3.68 (s, 6H), 2.98 (s, 3H), 2.79 (s, 3H). ^{13}C NMR (101 MHz, Chloro-form-*d*) δ 150.31, 133.45, 128.95, 128.69, 127.05, 125.52, 125.27, 120.37, 37.96, 36.08, 33.74. ^{11}B NMR (128 MHz, Chloro-form-*d*) δ −28.26 (t, *J* = 87.0 Hz). HRMS (ESI-TOF): *m/z* calculated for $C_{15}H_{21}BClN_3O_2S$ $[M + Na]^+$: 376.1018, found: 376.1021.

(*E*)-(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)(1-(4-fluorophenyl)-2-(*N*-methylmethylsulfonamido)vinyl)dihydroborate, **3f**: ^{1}H NMR (400 MHz, Chloro-form-*d*) δ 7.29–7.24 (m, 2H), 6.94–6.87 (m, 2H), 6.77 (s, 2H), 5.99 (s, 1H), 3.68 (s, 6H), 2.97 (s, 3H), 2.79 (s, 3H). ^{13}C NMR (126 MHz, Chloro-form-*d*) δ 161.37 (d, *J* = 243.3 Hz), 144.09 (d, *J* = 3.1 Hz), 128.36 (d, *J* = 7.5 Hz), 127.96, 120.31, 114.37 (d, *J* = 20.9 Hz), 37.95, 36.06, 33.64. ^{11}B NMR (128 MHz, Chloro-form-*d*) δ −28.21 (t, *J* = 86.7 Hz). ^{19}F NMR (376 MHz, Chloro-form-*d*) δ −118.36.

(*E*)-(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)(1-(3-fluorophenyl)-2-(*N*-methylmethylsulfonamido)vinyl)dihydroborate, **3g**: ^{1}H NMR (400 MHz, Chloro-form-*d*) δ 7.16 (td, *J* = 7.9, 6.2 Hz, 1H), 7.06 (dt, *J* = 7.7, 1.3 Hz, 1H), 7.03–6.98 (m, 1H), 6.85–6.79 (m, 1H), 6.76 (s, 2H), 6.04 (s, 1H), 3.68 (s, 6H), 2.98 (s, 3H), 2.79 (s, 3H). ^{13}C NMR (126 MHz, Chloro-form-*d*) δ 162.58 (d, *J* = 244.1 Hz), 150.83, (d, *J* = 7.4 Hz), 128.99, (d, *J* = 8.5 Hz), 128.60, 122.64 (d, *J* = 2.3 Hz), 120.35, 113.88 (d, *J* = 20.9 Hz), 112.22, (d, *J* = 21.2 Hz), 37.96, 36.08, 33.72. ^{11}B NMR (128 MHz, Chloro-form-*d*) δ −28.32 (t, *J* = 86.9 Hz). ^{19}F NMR (376 MHz, Chloro-form-*d*) δ −114.84.

(*E*)-(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)(1-(2-fluorophenyl)-2-(*N*-methylmethylsulfonamido)vinyl)dihydroborate, **3h**: ^{1}H NMR (400 MHz, Chloro-form-*d*) δ 7.13–7.02 (m, 2H), 6.97 (td, *J* = 7.4, 1.3 Hz, 1H), 6.91–6.85 (m, 1H), 6.75 (s, 2H), 6.03 (s, 1H), 3.64 (s, 6H), 3.06 (s, 3H), 2.82 (s, 3H). ^{13}C NMR (126 MHz, Chloro-form-*d*) δ 159.08 (d, *J* = 243.3 Hz), 135.75 (d, *J* = 16.2 Hz), 130.16 (d, *J* = 4.7 Hz), 129.58, 126.59 (d, *J* = 7.9 Hz), 123.33 (d, *J* = 3.4 Hz), 120.28, 115.01 (d, *J* = 23.3 Hz), 37.84, 35.93, 34.39. ^{11}B NMR (128 MHz, Chloro-form-*d*) δ −28.08, −28.08 (d, *J* = 175.1 Hz). ^{19}F NMR (376 MHz, Chloro-form-*d*) δ −116.94.

(*E*)-(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)(2-(*N*-methylmethylsulfonamido)-1-(4-(trifluoromethyl)phenyl)vinyl)dihydroborate, **3i**: ^{1}H NMR (400 MHz, Chloro-form-*d*) δ 7.47 (d, *J* = 8.0 Hz, 2H), 7.39 (d, *J* = 8.1 Hz, 2H),

6.78 (s, 2H), 6.03 (s, 1H), 3.68 (s, 6H), 2.98 (s, 3H), 2.79 (s, 3H). ^{13}C NMR (126 MHz, Chloro-form-*d*) δ 152.31, 128.99, 128.34 (q, *J* = 32.6 Hz), 127.23, 125.88 (q, *J* = 270.2 Hz), 124.62 (q, *J* = 3.8 Hz), 120.41, 37.93, 36.08, 33.66. ^{11}B NMR (128 MHz, Chloro-form-*d*) δ −28.21 (t, *J* = 86.8 Hz). ^{19}F NMR (376 MHz, Chloro-form-*d*) δ −62.09.

(*E*)-(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)(1-(4-(methoxycarbonyl)phenyl)-2-(*N*-methylmethylsulfonamido) vinyl)dihydro-borate, 3j: ^{1}H NMR (400 MHz, Chloro-form-*d*) δ 7.89–7.85 (m, 2H), 7.34–7.30 (m, 2H), 6.73 (s, 2H), 6.07 (s, 1H), 3.87 (s, 3H), 3.66 (s, 6H), 3.01 (s, 3H), 2.80 (s, 3H). ^{13}C NMR (101 MHz, Chloro-form-*d*) δ 167.43, 153.72, 129.18, 129.03, 127.21, 127.03, 120.38, 51.95, 37.98, 36.09, 33.91. ^{11}B NMR (128 MHz, Chloro-form-*d*) δ −28.22 (t, *J* = 86.9 Hz).

(*E*)-(1-(4-cyanophenyl)-2-(*N*-methylmethylsulfonamido)vinyl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydro-borate, 3k: ^{1}H NMR (400 MHz, Chloro-form-*d*) δ 7.50–7.46 (m, 2H), 7.40–7.34 (m, 2H), 6.76 (s, 2H), 6.01 (s, 1H), 3.65 (s, 6H), 2.94 (s, 3H), 2.76 (s, 3H). ^{13}C NMR (101 MHz, Chloro-form-*d*) δ 153.76, 131.63, 129.45, 127.77, 120.49, 119.59, 108.92, 37.90, 36.11, 33.67. ^{11}B NMR (128 MHz, Chloro-form-*d*) δ −28.23 (t, *J* = 87.1 Hz). HRMS (ESI-TOF): *m/z* calculated for $C_{16}H_{21}BN_4O_2S$ [M + Na]$^+$:367.1378, found:367.1363.

(*E*)-(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)(1-(4-methoxyphenyl)-2-(*N*-methylmethylsulfonamido)vinyl)dihy-droborate, 3L: ^{1}H NMR (400 MHz, Chloro-form-*d*) δ 7.25–7.21 (m, 2H), 6.76–6.72 (m, 2H), 6.71 (s, 2H), 5.94 (s, 1H), 3.74 (s, 3H), 3.64 (s, 6H), 2.92 (s, 3H), 2.74 (s, 3H). ^{13}C NMR (101 MHz, Chloro-form-*d*) δ 157.90, 140.57, 128.04, 127.28, 120.23, 113.18, 55.27, 37.98, 36.09, 33.60. ^{11}B NMR (128 MHz, Chloro-form-*d*) δ −28.27 (t, *J* = 86.4 Hz). HRMS (ESI-TOF): *m/z* calculated for $C_{16}H_{24}BN_3O_3S$ [M + Na]$^+$: 372.1515, found: 372.1517.

(*E*)-(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)(2-(*N*-methylmethylsulfonamido)-1-(*p*-tolyl)vinyl)dihydroborate, 3m: ^{1}H NMR (400 MHz, Chloro-form-*d*) δ 7.21 (d, *J* = 8.1 Hz, 2H), 7.03 (d, *J* = 7.6 Hz, 2H), 6.75 (s, 2H), 6.00 (s, 1H), 3.68 (s, 6H), 2.96 (s, 3H), 2.78 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, Chloro-form-*d*) δ 145.23, 135.06, 128.43, 127.65, 126.89, 120.22, 37.94, 36.06, 33.62, 21.04. ^{11}B NMR (128 MHz, Chloro-form-*d*) δ −28.24 (t, *J* = 86.4 Hz).

(*E*)-(1-(4-(*tert*-butyl)phenyl)-2-(*N*-methylmethylsulfonamido)vinyl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)di-hydroborate, 3n: ^{1}H NMR (400 MHz, Chloro-form-*d*) δ 7.19 (d, *J* = 2.1 Hz, 4H), 6.69 (s, 2H), 5.93 (s, 1H), 3.62 (s, 6H), 2.86 (s, 3H), 2.69 (s, 3H), 1.22 (s, 9H). ^{13}C NMR (101 MHz, Chloro-form-*d*) δ 148.42, 145.07, 127.62, 126.63, 124.60, 120.22, 37.94, 36.08, 34.32, 33.37, 31.44. ^{11}B NMR (128 MHz, Chloro-form-*d*) δ −28.27 (t, *J* = 86.3 Hz).

(*E*)-(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)(2-(*N*-methylmethylsulfonamido)-1-(naphthalen-2-yl)vinyl)dihydro-borate, 3o: ^{1}H NMR (400 MHz, Chloro-form-*d*) δ 7.79–7.68 (m, 4H), 7.51 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.44–7.35 (m, 2H), 6.73 (s, 2H), 6.16 (s, 1H), 3.70 (s, 6H), 3.05 (s, 3H), 2.83 (s, 3H). ^{13}C NMR (101 MHz, Chloro-form-*d*) δ 145.96, 133.58, 132.05, 128.60, 127.77, 127.49, 127.00, 126.73, 125.61, 124.84, 124.50, 120.29, 38.06, 36.14, 33.81. ^{11}B NMR (128 MHz, Chloro-form-*d*) δ −27.83 (d, *J* = 87.0 Hz). HRMS (ESI-TOF): *m/z* calculated for $C_{19}H_{24}BN_3O_2S$ [M + Na]$^+$: 392.1582, found: 392.1567.

(*E*)-(1-([1,1′-biphenyl]-4-yl)-2-(*N*-methylmethylsulfonamido)vinyl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)di-hydroborate, 3p: ^{1}H NMR (400 MHz, Chloro-form-*d*) δ 7.61–7.42 (m, 4H), 7.40 (dd, *J* = 8.1, 3.7 Hz, 4H), 7.31 (d, *J* = 14.7 Hz, 1H), 6.76 (s, 2H), 6.09 (s, 1H), 3.71 (s, 6H), 2.99 (s, 3H), 2.81 (s, 3H). ^{13}C NMR (101 MHz, Chloro-form-*d*) δ 147.40, 141.25, 138.42, 128.70, 128.10, 127.49, 126.91, 126.49, 120.31, 38.02, 36.15, 33.61. ^{11}B NMR (128 MHz, Chloro-form-*d*) δ −28.20 (t, *J* = 86.4 Hz).

(*E*)-(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)(2-(*N*-methylmethylsulfonamido)-1-(thiophen-2-yl)vinyl)dihydro-borate, 3q: ^{1}H NMR (400 MHz, Chloro-form-*d*) δ 7.26 (d, *J* = 2.2 Hz, 1H), 7.18 (d, *J* = 2.2 Hz, 2H), 6.77 (s, 2H), 6.23 (s, 1H), 3.69 (s, 6H), 2.92 (s, 3H), 2.77 (s, 3H). ^{13}C NMR (101 MHz, Chloro-form-*d*) δ 147.96, 127.39, 126.86, 124.41, 120.39, 120.31, 37.91, 36.12, 33.56. ^{11}B NMR (128 MHz, Chloro-form-*d*) δ −28.60 (t, *J* = 86.2 Hz).

(*E*)-(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)(1-(*N*-methylmethylsulfonamido)pent-1-en-2-yl)dihydroborate, 3r: ^{1}H NMR (400 MHz, Chloro-form-*d*) δ 6.80 (s, 2H), 5.66 (s, 1H), 3.72 (s, 6H), 2.75 (s, 3H), 2.69 (s, 3H), 2.04 (t, *J* = 7.5 Hz, 2H), 1.55–1.48 (m, 2H), 0.87 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, Chloro-form-*d*) δ 124.53,

120.15, 42.55, 37.99, 36.03, 32.86, 22.27, 14.17. **^{11}B NMR (128 MHz, Chloro-form-*d*)** δ −29.02 (t, *J* = 84.6 Hz). **HRMS (ESI-TOF)**: *m/z* calculated for $C_{12}H_{24}BN_3O_2S$ $[M + Na]^+$: 308.1582, found: 308.1569.

(*E*)-(6-chloro-1-(*N*-methylmethylsulfonamido)hex-1-en-2-yl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate, **3s**: **^{1}H NMR (400 MHz, Chloro-form-*d*)** δ 6.81 (s, 2H), 5.67 (s, 1H), 3.72 (s, 6H), 3.55 (t, *J* = 6.8 Hz, 2H), 2.74 (s, 3H), 2.68 (s, 3H), 2.09 (t, *J* = 7.4 Hz, 2H), 1.81–1.72 (m, 2H), 1.63 (q, *J* = 8.4 Hz, 2H). **^{13}C NMR (101 MHz, Chloro-form-*d*)** δ 124.78, 120.21, 45.49, 39.52, 37.98, 36.04, 32.85, 32.67, 26.41. **^{11}B NMR (128 MHz, Chloro-form-*d*)** δ −29.09 (t, *J* = 85.0 Hz). **HRMS (ESI-TOF)**: *m/z* calculated for $C_{13}H_{25}BClN_3O_2S$ $[M + Na]^+$: 356.1338, found: 356.1334.

(*E*)-(1-cyclopropyl-2-(*N*-methylmethylsulfonamido)vinyl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate, **3t**: **1H NMR (400 MHz, Chloro-form-*d*)** δ 6.79 (s, 2H), 5.73 (s, 1H), 3.71 (s, 6H), 2.74 (s, 3H), 2.68 (s, 3H), 1.44 (s, 1H), 0.81–0.67 (m, 2H), 0.62–0.48 (m, 2H). **^{13}C NMR (101 MHz, Chloro-form-*d*)** δ 123.28, 120.19, 37.89, 36.06, 32.70, 19.06, 5.31. **^{11}B NMR (128 MHz, Chloro-form-*d*)** δ −31.20 (t, *J* = 84.5 Hz).

(*E*)-(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)(1-(*N*-methylmethylsulfonamido)-4-phenylbut-1-en-2-yl)dihydroborate, **3u**: **^{1}H NMR (400 MHz, Chloro-form-*d*)** δ 7.24–7.17 (m, 4H), 7.13–7.08 (m, 1H), 6.77 (s, 2H), 5.54 (s, 1H), 3.70 (s, 6H), 2.81–2.76 (m, 2H), 2.64 (s, 3H), 2.57 (s, 3H), 2.34 (t, *J* = 7.8 Hz, 2H). **^{13}C NMR (101 MHz, Chloro-form-*d*)** δ 143.46, 128.75, 128.01, 125.32, 125.16, 120.20, 42.51, 37.82, 36.06, 35.73, 32.80. **^{11}B NMR (128 MHz, Chloro-form-*d*)** δ −28.91 (t, *J* = 84.9 Hz).

(*Z*)-*N*-(2-(4-acetylphenyl)-2-phenylvinyl)-*N*-methylmethanesulfonamide, **5a**: **^{1}H NMR (400 MHz, Chloro-form-*d*)** δ 7.98 (d, *J* = 8.3 Hz, 2H), 7.38 (d, *J* = 8.3 Hz, 2H), 7.32–7.27 (m, 3H), 7.17–7.12 (m, 2H), 6.83 (s, 1H), 2.96 (s, 3H), 2.72 (s, 3H), 2.64 (s, 3H). **^{13}C NMR (101 MHz, Chloro-form-*d*)** δ 197.56, 143.49, 140.28, 136.43, 131.33, 130.55, 128.49, 128.44, 127.91, 126.72, 37.51, 36.70, 26.69.

(*Z*)-*N*-(2-(4-cyanophenyl)-2-phenylvinyl)-*N*-methylmethanesulfonamide, **5b**: **^{1}H NMR (400 MHz, Chloro-form-*d*)** δ 7.69 (d, *J* = 8.3 Hz, 2H), 7.41 (d, *J* = 8.3 Hz, 2H), 7.33–7.28 (m, 3H), 7.12 (dd, *J* = 6.9, 2.9 Hz, 2H), 6.80 (s, 1H), 2.96 (s, 3H), 2.74 (s, 3H). **^{13}C NMR (101 MHz, Chloro-form-*d*)** δ 143.39, 139.80, 132.25, 131.02, 128.56, 128.19, 127.97, 127.22, 118.56, 111.69, 37.31, 36.87.

Further details can be found in the accompanying supplemental information.