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Copper-boryl mediated transfer hydrogenation of *N*-sulfonyl imines using methanol as the hydrogen donor

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ABSTRACT

B_2Pin_2-assisted copper-catalyzed transfer hydrogenation of aromatic sulfonylimines has been achieved, delivering a variety of aryl/heteroaryl sulfonamides in good to excellent yields under mild reaction conditions and with methanol as the hydrogen source. Mechanistic studies suggest that the reaction may proceed via a transient α-borylated intermediate, followed by protodeboration to afford the sulfonamide products.

1. Introduction

The sulfonamide motif characterizes the structure of numerous biologically active compounds (Fig. 1), including the early sulfa antibiotics (e.g. **1**) [1], the HIV antivirals amprenavir (**2**) and darunavir (**3**), as well as pre-clinical exploratory compounds, such as the antitumor agent **4** [2], and the γ-secretase inhibitor **5** [3]. One of the most frequently used methods for the synthesis of sulfonamides is the direct sulfonylation of amines with sulfonyl chlorides in the presence of a base [4]. However, this method requires the handling of chemically unstable sulfonyl chlorides. The metal-catalyzed reaction of sulfonamides with unreactive alcohols (the so-called borrowing hydrogen reaction) is an alternative approach [5].

Although this method is often described as atom economical, it usually requires the use of precious transition metals (typically Ru, Rh, Ir) and harsh reaction conditions (typically >100 °C) [6]. Asymmetric hydrogenation of *N*-sulfonyl imines catalyzed by Ni [7] or co-catalyzed by Pd/$Zn(OTf)_2$ [8] have also been reported, using high-pressures of H_2 gas.

Transfer hydrogenations of *N*-sulfonyl imines using HCOOH, HCO_2NH_4, simple alcohols or water as the proton source, and catalyzed by transition metals, provide noteworthy advantages (Scheme 1a-c) [9]. Despite these notable advances, the use of toxic transition metals that are found in low-abundance in Nature (Pd, Rh or Ir) is still a concern, especially when used in the production of human therapeutics.

During preparation of this manuscript, the Ni-catalyzed asymmetric transfer hydrogenation of *N*-sulfonyl imines was reported (Scheme 2a) [10]. It stands to reason that when earth-abundant metals can catalyze such transfer hydrogenations, using simple alcohols or water, such methodologies are both greener and more economical. Mindful of this, we began to explore the Cu-mediated transfer hydrogenation of *N*-sulfonyl imines. Examples of similar methods have been previously employed in the copper-boryl mediated transfer hydrogenations of alkenes and alkynes [11], the chemoselective reduction of conjugated α,β-unsaturated ketones [12], and the semihydrogenation of alkynes to the *Z*-alkenes [13]. In this report, we describe the copper-boryl mediated transfer hydrogenation of sulfonyl imines to the corresponding sulfonamides using methanol as the proton source at room temperature and in good to excellent yields (Scheme 2b).

2. Results and discussion

Our investigations commenced by examining the copper-boryl mediated transfer hydrogenation of (*E*)-*N*-benzylidene-4-bromobenzenesulfonamide (**6a**) as the model substrate under a variety of reaction conditions (Table 1). Initially, a trace amount of the desired sulfonamide **7a** was obtained, when **6a** was treated with CuCl (10 mol %) and bis(pinacolato)diboron (B_2pin_2; 0.1 equiv.)

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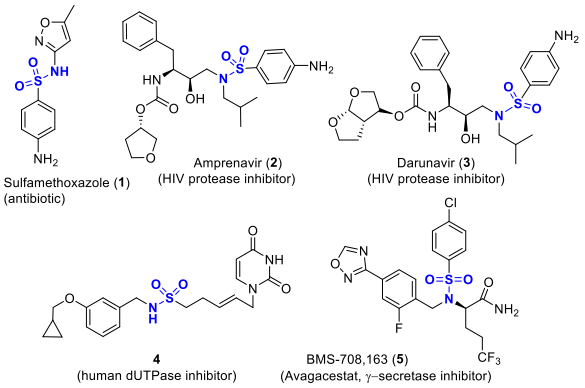
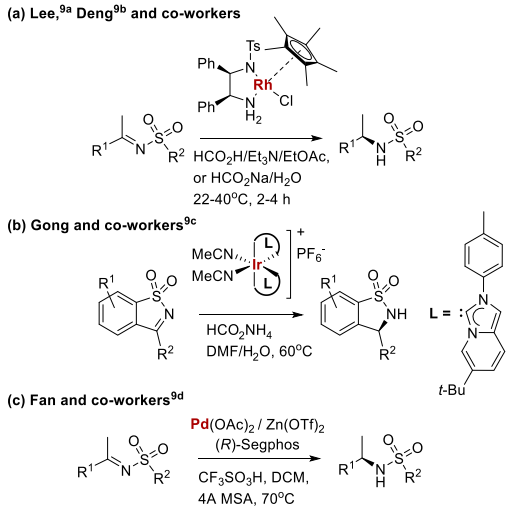
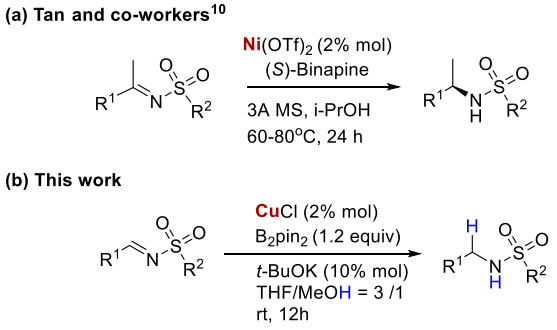


Fig. 1. Biologically active sulfonamide.



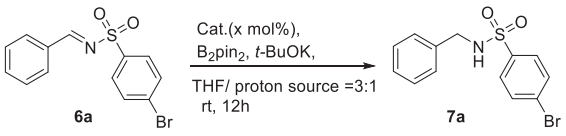
Scheme 1. Transfer hydrogenation of sulfonyl imines catalyzed by second and third row transition metals.



Scheme 2. Transfer hydrogenation of sulfonyl imines catalyzed by first-row transition metals.

under basic conditions at room temperature (entry 1). However, sequentially increasing the amount of B_2pin_2 (from 0.1 to 1.2 equiv.) results in parallel successive increase in yields of the desired product **7a** from 6% to 65% (entries 1–3). Interestingly, other copper salts, including CuBr (entry 4) and $Cu(acac)_2$ (entry 5), had a slight detrimental effect in the reaction yield, whereas, decreasing the amount of base by 10-fold or the amount of CuCl by 2-fold did not affect the outcome, leading to nearly quantitative yields (entry 3 vs

Table 1
Optimization of reaction conditions[a].



entry	Catalyst (mol%)	B_2Pin_2 (equiv)	proton source	Base (equiv)	7a[c] % yield
1	CuCl(10)	0.1	MeOH	0.1	6
2	CuCl(10)	0.5	MeOH	0.1	34[b]
3	CuCl(10)	1.2	MeOH	1	65
4	CuBr(10)	1.2	MeOH	1	55
5	$Cu(acac)_2$(10)	1.2	MeOH	1	58
6	$Pd(OAc)_2$(10)	1.2	MeOH	1	5
7	CuCl(10)	1.2	MeOH	0.1	100[b]
8	CuCl(5)	1.2	MeOH	0.1	98
9	CuCl(5)	1.2	EtOH	0.1	90[b]
10	CuCl(5)	1.2	*i*-PrOH	0.1	62[b]
11	CuCl(5)	1.2	H_2O	0.1	73[b]
12[d]	–	1.2	MeOH	0.1	0
13[e]	CuCl(5)	1.2	–	0.1	0
14[f]	CuCl(5)	1.2	MeOH	–	0
15[g]	CuCl(5)	1.2	MeOH	0.1	75
16[h]	CuCl(5)	1.2	MeOH	0.1	45[b]

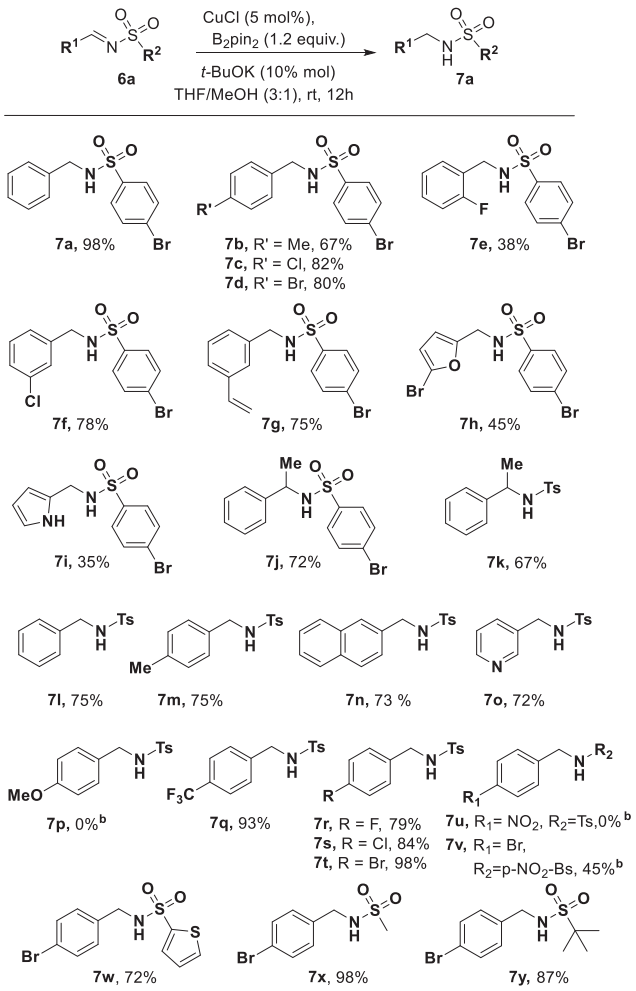
[a] Reactions were carried out on a 0.1 mmol scale of **1a** under the protection of Argon.
[b] Yield was estimated by ^{1}HNMR using CH_2Br_2 as internal standard.
[c] Isolated yield.
[d] Without CuCl.
[e] Without MeOH.
[f] Without *t*-BuOK.
[g] without THF.
[h] Under air.

entries 7 and 8, respectively). Additionally, under these same reaction conditions, $Pd(OAc)_2$, failed to catalyze this reaction to any appreciable amount (entry 6). Screening of simple alcohols and water suggested that methanol was the best hydrogen source (entries 8–11), whereas, the reaction did not proceed at all in the absence of Cu^{+1}, a proton source or *t*-BuOK (entries 12–14). Exposure of the reaction mixture to air resulted in significantly lower yield (entry 16), consistent with an air-sensitive copper species (a Cu–H or a change in oxidation state of Cu^{+1}) that may be generated in the course of this reaction. The generation of such a species was previously reported for related Cu–H and Cu–B mediated reactions involving alkynes [11].

Subsequently, we sought to investigate the generality of this methodology and substrate scope. A range of *N*-sulfonyl imines **6**, readily synthesized from substituted benzaldehydes or heterocyclic aldehydes and 4-bromobenzenesulfonamides (**6a-6i**), were subjected to the same reaction conditions (in a parallel library mode) to give the desired products **7a-7i** (Table 2).

Both *para*- and *meta*-substituted *N*-benzylic moieties (**7a-7d**, **7f** and **7g**) were obtained in good to excellent yields. Lower yields were obtained with *N*-substituents having an *ortho*-fluoro moiety (**7e**) or a heterocyclic substituent with a strongly electronegative atom at the Cβ carbon (**7h** and **7i**). This is likely due to the coordination effect of these heteroatoms with the copper cation to form a stable 5-membered ring intermediate that decelerates the reaction rate. *N*-Sulfonyl imines derived from ketones were also viable substrates in this reaction, providing the desired products **7j** and **7k** in fairly good yields (72% and 67%, respectively). *N*-Sulfonyl imines obtained from the condensation of *p*-toluenesulfonamide and various substituted benzaldehyde were also explored. Reactions

Table 2
Substrate Scope of the B_2Pin_2-assisted Copper-catalyzed Transfer Hydrogenation of Aryl/Heteroaryl *N*- Sulfonyl Imines [a].

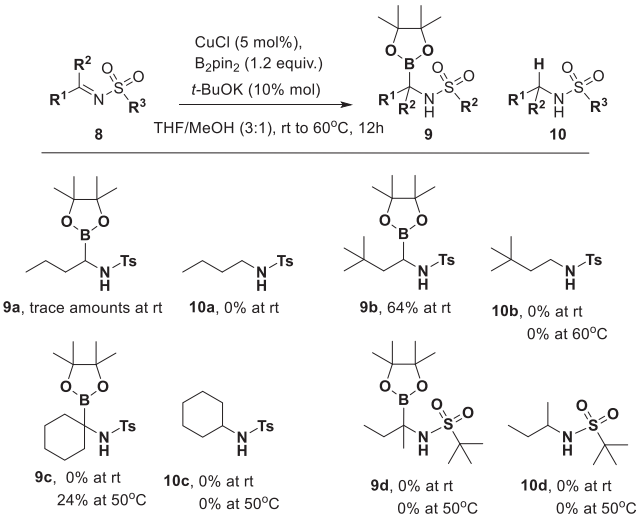


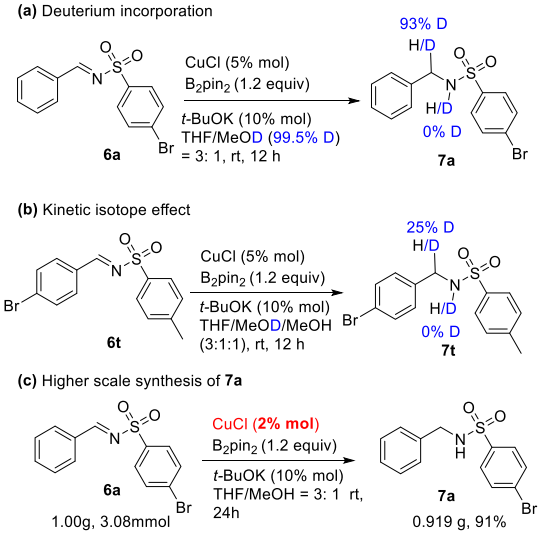
with aldimines bearing a benzylic substituent, including electron-rich arenes (e.g. **7m** and **7n**), heterocycles (**7o**) and those having an electron-withdrawing group at the *para* position (e.g. **7q**-**7t**), proceeded efficiently and in good to excellent yields. Electron withdrawing substituents would be expected to activate the imine carbon for nucleophilic attack. However, we were unsuccessful in obtaining the nitro analog **7u** and a fairly modest yield was obtained of **7v**, possibly due to coordination and deactivation of the copper cation by the nitro group. Strongly electron-donating substituents, such as a *para*-methoxy group, would be expected to decelerate nucleophilic attach on the imine carbon and consequently, act as poor substrates for this type of reaction (e.g. **7p**; no conversion was observed with imine **6p** even at higher temperature and prolonged reaction time). Finally, some structural diversity on the sulfur substitution was also explored; examples included a thiophene, methyl and *tert*-butyl moiety, all of which gave good to excellent yields of the desired product (**7w**, **7x** and **7y**, respectively).

We subsequently explored the application of this methodology in the transfer hydrogenation of aliphatic aldimines and ketimines (Table 3). Surprisingly, when sulfonylimines **8** were treated under the above optimized conditions (Table 3), we did not observe any of the desired products **10**; in most cases, unreacted starting material and some decomposition products were recovered. In a few cases, modest yields of the Cα borylated products **9** were observed from aldimine-based substrates (e.g. **9b**). Similar results were also observed with ketimines-based substrates, but only at higher temperatures (e.g. **9c**). It is noteworthy that even when the purified borylated products **9** were re-exposed to the same reaction conditions at 60 °C for an additional 15h, only unreacted starting material was observed. Asymmetric *N*-heterocyclic carbene (NHC)–Cu-catalyzed or NHC-metal free synthesis of α-amino boronate esters from sulfinamide substrates were previously reported by Ellman [14] and Sun [15]. However, Ellman reported that α-amino boronate esters of aromatic aldimines were chemically unstable and protodeborylation of such analogs occurred rapidly during chromatography [14a], particularly for those analogs with electron withdrawing substituent (*e.g.* the corresponding sulfinamide analog of sulfonamide **6q**; Table 2). Given the expected higher electron deficiency of the C=N bond in sulfonamides, it is reasonable to assume that their corresponding α-amino boronate esters will be highly chemically unstable; reports of such compounds are rare in the literature [16].

To gain more insight into the mechanism of this reaction, a number of deuterium-labelling experiments were carried out (Scheme 3). Replacement of MeOH by MeOD (99.5% D enriched) in the reaction of **6a** under standard conditions, lead to selective incorporation of deuteride to the imine-carbon of **6a**, affording deuterium-labelled **7a** in 90% yield and approximately 93%

Table 3
Examples of the B_2Pin_2-assisted Copper-catalyzed Borylation of Aliphatic *N*-Sulfonyl Imines and Ketimines [a].



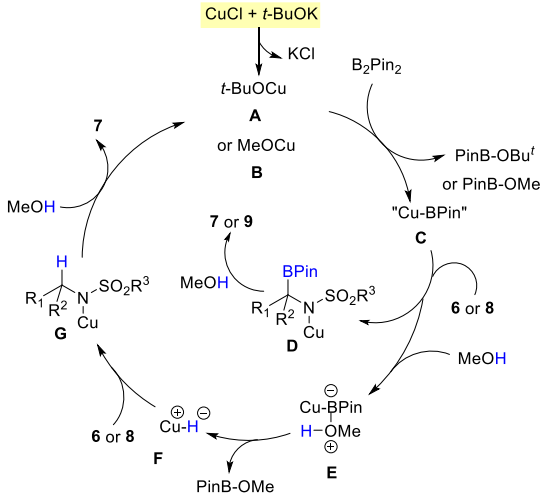


Scheme 3. Deuterium-labelling experiments.

deuterium content (Scheme 3a). The incorporation of deuterium was confirmed by ^2H NMR and the % incorporation was estimated from the ^1H NMR integrations of the methylene signal. This result is be consistent with methanol acting as the hydrogen donor in this reaction. In recent years, isotope labelling has drawn significant attention as an application in deuterated drugs [17], and this methodology can efficiently provide high deuteride incorporation under mild reaction conditions. Next, we employed an equal mixture of MeOH and MeOD (99.5% D enriched) to investigate the existence of any kinetic isotope effect. Compound **6t** was subjected to the same reaction conditions and **7t** was obtained in 88% yield and approximately 25% deuteride incorporation on the carbon (Scheme 3b). It is estimated that the kinetic isotope effect (KIE) of the reaction kH/kD is approximately 3, suggesting that the O–H bond cleavage of MeOH is the rate-determining step. To further shed light on the practical use of this method, a gram-scale reaction was performed using **6a** as the substrate and only 2 mol% of CuCl to obtain **7a** in 91% isolated yield (Scheme 3c).

Based on the above experiments and previous reports [11a,b,12,13,18], a plausible mechanism for this copper-boryl mediated transfer hydrogenation reaction is proposed in Scheme 4. The alkoxy copper species **A** is first formed by the reaction of CuCl and *t*-BuOK. The reaction of **A** with B_2Pin_2 produces the Cu–boron complex **C**, which subsequently reacts with the C=N bond to give the α-borylated intermediate complex **D**, followed by protodeborylation with methanol.

To account for the differences observed in the products formed from the aromatic (**6**) vs the aliphatic (**8**) substrates, we followed the transfer hydrogenation reaction of *N*-sulfonyl imine **6a** in the presence of nearly stoichiometric amounts of all reagents (B_2pin_2, CuCl and *t*-BuOK) by ^1H NMR at room temperature (Fig. 2). It should be noted that the ^1H NMR spectrum of compound **6a** (Fig. 2) shows two sets of peaks, the smaller set of peaks belongs to the hemi-aminal, which is formed from the nucleophilic addition of MeOH to the imine; however, this equilibrium does not affect the progress, nor outcome of the reaction. A transient intermediate was almost immediately observed (Fig. 2; t = 0), which disappeared after



Scheme 4. Plausible mechanisms.

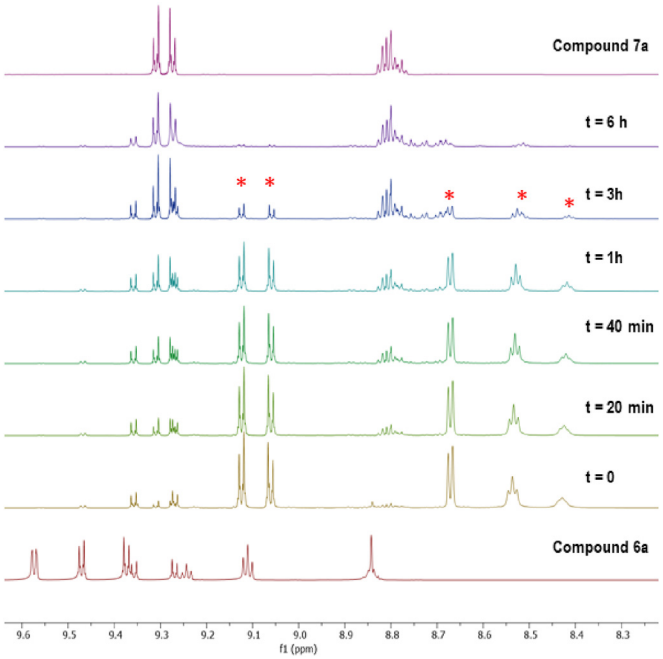


Fig. 2. ^{1}H NMR (800 MHz) of the transfer hydrogenation reaction of **6a** in THF-d8/methanol-d4 (3:1) mixture.

approximately 4 h leading to the formation of product **7a**. This observation suggests the formation of an unstable borylated species for the aromatic substrates.

Although less likely, we cannot exclude the possibility of a competing mechanism involving coordination of MeOH with the Cu-Bpin compex to generate the complex **E**, leading to the generation of the copper hydride species **F**. The nucleophilic addition of the hydride to the C=N double bond of *N*-sulfonyl imines **6** can afford the cuprate intermediate **G**, which upon methanol-mediated proton decupration delivers **7**, with a concomitant regeneration of the active catalyst. Analogous results have been reported by Lipshutz in the Cu−H asymmetric hydrosilylation of diphenylphosphinyl imines, where the phosphinyl moiety was specifically selected in order to weaken the Cu−N bond, prior to the transmetalation step and the regeneration of the metal catalyst [19].

3. Conclusion

In summary, we have developed an efficient copper-boryl mediated transfer hydrogenation protocol that can provide diverse aryl/heteroaryl sulfonamides in good to excellent yields under mild reaction conditions. Moreover, the utility of an inexpensive copper catalyst and a simple alcohol as the hydrogen source represent an economical and green method for this transfer hydrogenation reaction. Further optimization of this method into an asymmetric transfer hydrogenation should be possible and will be investigated in the near future.

4. Materials and methods

4.1. General information

NMR spectra were recorded in $CDCl_3$, unless otherwise indicated, and chemical shifts are reported in ppm relative to the deuterated solvent. HRMS were obtained on a TOF instrument by electrospray ionization positive and negative modes (ESI±). The quoted masses are accurate to ±5 ppm. Completion of all reactions was monitored by thin-layer chromatography (TLC), and LCMS. Flash column chromatography was performed on silica gel (SDS, 60 Å C. C. 40−63 mm) as the stationary phase. TLC was performed on alumina plates precoated with silica gel (Merck silica gel, 60 F254), which was visualized by the quenching of UV fluorescence when applicable (λmax = 254 nm and/or 366 nm). All starting materials purchased from commercial suppliers were used without further purification except benzaldehyde which was distilled. 4 Å Molecular sieves, 1.6−2.5 mm of particle size, were activated by flame drying for 30 s twice.

4.2. Preparation of the N-sulfonyl imines 6a-6i, 6l-6y

[18] In a pressure vial (25 mL), molecular sieves 4 Å (1 g/mol) were added and framed dried for 30 s twice. After cooling down under Ar, aldehyde (2.1 mmol), pyrrolidine (0.17 mmol) and *p*-toluenesulfonamide (1.75 mmol) were added, then anhydrous DCM (3 mL) was added. The mixture was stirred at 60 °C overnight. The reaction was filtered through a short pad of Celite and washed with EtOAc, the solvent was then evaporated under reduced pressure and the residue was recrystallized with ethyl acetate/petroleum ether (20:80) to obtain the desired *N*-sulfonylimines. Due to the chemical instability of these compounds on silica gel, most were used directly after only minimal purification.

4.3. Preparation of the N-sulfonyl imines 6j, 6k

A 25 mL pressure vial equipped with a stirring bar was charged with aldehyde (2.1 mmol), sulfonamide (1.9 mmol), anhydrous toluene (5 mL), and $Ti(OEt)_4$ (3.8 mmol). The vial was closed and heated at 50 °C for 12h. After completion, the mixture was cooled to room temperature and extracted with EtOAc. The combined organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel with EtOAc/Hexane (v/v, 1/2) to afford the compounds **6j** and **6k** as a yellow oil.

4.4. Preparation of the N-sulfonyl imines 8a and 8b

Aldimines **8a** and **8b** were prepared using the method previously reported by Cid with minor modifications [20].

4.5. General procedure of transfer hydrogenation of N-sulfonyl imines

The starting material *N*-sulfonyl imines **6** (0.2 mmol), CuCl (5 mol %) and bis(pinacolato)diboron (1.2 equiv.), *t*-BuOK (10 mol %) were placed in oven-dried round bottom flask (10 mL) closed with a septum, the vials were connected to a vacuum/Ar manifold through a needle, evacuated and then back filled with Ar for three times. Regular THF (0.9 mL) was added via a syringe, then MeOH (0.3 mL) was added dropwise and the mixtures were stirred at room temperature for 12 h. The residues obtained were purified by column chromatography on silica gel with EtOAc/Hexane (v/v, 1/3) to provide the desired products **7** as solids.

4.6. Gram scale reaction of 7a

The starting material *N*-sulfonyl imine **6a** (1.0 g, 3.09 mmol), CuCl (6.13 mg, 2 mol %) and bis(pinacolato)diboron (0.93 g, 1.2 equiv.), *t*-BuOK (68 mg, 10 mol %) were placed in an oven-dried round bottom flask (50 mL) and sealed with a septum. The vial was connected to a vacuum/Ar manifold through a needle, it was evacuated and then back filled with Ar for three times. Then THF (3 ml) was added by syringe. Subsequently, the MeOH (1 mL) was

added drop wisely. After completion (24h), the residue obtained was purified by column chromatography on silica gel with EtOAc/Hexane (v/v, 1/3) to provide the desired products **7a** as solid (0.919 g, 91% yield).

Except for compounds **6d, 6e, 6f, 6g, 6h, 7e, 7f, 7g, 7h, 7i, 7w, 7y**, all other compounds were characterized by comparing their ^{1}H and ^{13}C NMR spectra with reported literature data; relevant references can be found in the supporting information.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.tet.2021.132063.

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