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Bis(trifluoromethanesulfonimide) (BSI): Acidity and application to hydrofunctionalization as a Brønsted acid catalyst

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ABSTRACT

A binaphthyl derivative, bearing bis(trifluoromethanesulfonimide) (BSI) moiety, was developed as a novel Brønsted acid. Computational prediction of the pK_a value of BSI indicated its classification as a strong Brønsted acid. BSI catalyzed the hydroamination of alkenyl amines in hexafluoroisopropanol (HFIP) with efficiency comparable to that of TsOH·H_2O, Tf_2NH, and TfOH. The adjacent sulfonimide groups on BSI were important for enhancing acidity. BSI additionally catalyzed the hydroalkoxylation of alkenyl alcohols in HFIP with high efficiency.

1. Introduction

Brønsted acids have recently emerged as a significant tool in metal-free catalysis for a range of organic synthetic reactions [1]. Owing to their acidity, they are principally used to activate basic substrates bearing nitrogen-containing nucleophiles, including aldimines, ketimines, and aziridines, while harsh reaction conditions are required for the activation of less basic substrates, such as alkenes and alkynes [2]. Therefore, although several asymmetric hydrofunctionalization reactions of alkenyl derivatives catalyzed by chiral Brønsted acids have been developed [3], only three examples (hydroamination of alkenyl [4] or dienyl amines [5], and hydroalkoxylation of alkenyl alcohol [6]) have been reported to occur via direct activation of the alkene moiety of alkenyl derivatives.

Thus far, two strategies have been applied to overcome acidity limitations and create a strong chiral Brønsted acid [7]. The introduction of strongly electron-withdrawing groups, such as *N*-triflyl phosphoramide [7h], disulfonimide [7e,8], imidodiphosphate [7d,9] and imidodiphosphorimidate [7a,6] onto the chiral binaphthol (BINOL) skeleton is one strategy. Another relies on stabilization of the conjugate base of the Brønsted acid by intramolecular hydrogen bonding from the adjacent functional group. Based on the latter strategy, chiral Brønsted acids bearing two strongly electron-withdrawing groups, such as dicarboxylic acid [10], disulfonic acid [7g,11], diphosphoric acid [12], tether-linked diphosphoric acid [13] and conjugate-base-stabilized carboxylic acids [14] have been developed. Terada and co-workers employed X-ray diffraction analysis to reveal intramolecular hydrogen bonding between the two phosphoric acid moieties in diphosphoric acid [13d]. This suggests that intramolecular hydrogen bonding in a Brønsted acid bearing two adjacent strongly electron-withdrawing groups could play an important role in attaining high reactivity and stereoselectivity. We focused on bis(trifluoromethanesulfonyl)imide (triflimide: Tf_2NH), a super Brønsted acid [15], and designed a BINOL-derived Brønsted acid bearing bis(trifluoro methanesulfonimide) group at the 2,2′-positions (BSI) **1** (Fig. 1). In this report, the preparation method of **1** and its application to the hydrofunctionalization of alkenyl amines and alcohols as a Brønsted acid are described.

2. Results and discussion

BSI (**1**) was synthesized by reaction of trifluoro methanesulfonamide with the sulfonyl chloride intermediate, which was prepared from chiral BINOL via Suzuki–Miyaura coupling, Newman–Kwart rearrangement, oxidation, and chlorination, according to List's procedure (non-substituted sulfonimide **1a** was synthesized from racemic-BINOL) (Scheme 1) [8b], [c],

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[11c,16]. Although non-substituted sulfonimide **1a** was deliquescent akin to Tf_2NH, 3,3′-substituted sulfonimides **1b** and **c** were not.

To evaluate the acidic strength of sulfonimide **1**, the pK_a value of sulfonimide **1a** in DMSO has been predicted by a computational study using the direct method at the SMD/M06-2x/6−311++G(2df,2p)//B3LYP/6-31+G(d) level of theory (Fig. 2) [17]. The predicted pK_a value (−5.26) of **1a** suggested that sulfonimide **1** is one of the stronger acids among the known BINOL-derived Brønsted acids, including disulfonic acid (BINSA), *N*-trifylphosphoramide (NTPA), sulfuryl imides (JINGLE) and disulfonimide (DSI). The optimized structure of **1a** and its conjugate base indicated that the intramolecular hydrogen bonding between the two sulfonimides plays an important role in enhancing acidity.

Having assessed the acidity of sulfonimides **1**, their efficiency as catalysts in the intramolecular hydroamination of alkenyl amine **2a** was evaluated (Table 1). The hydroamination reaction was conducted in CH_2Cl_2 at 40 °C for 7 days indicated that the acidity of sulfonimides **1a** and **1b** was insufficient for the reaction (entries 1 and 2). The introduction of a CF_3 group on the 3,3′-substituents enhanced the reactivity of sulfonimide **1c**, and pyrrolidine **3a** was obtained in good yield (81% yield, entry 3). Such a reactivity enhancement achieved by the introduction of an electron-withdrawing group accords with the computational pK_a prediction by Li and Cheng [17]. When benzene was used as the solvent, the chemical yield was slightly decreased (entry 4). In order to improve the efficiency of the reaction, polyfluorinated alcohols were used as the solvent due to their unique properties, including their protic and non-nucleophilic character, excellent hydrogen bonding donor ability, high ionizability beneficial for stabilizing cationic species, and high polarity (entries 5–7) [18]. The hydroamination reaction proceeded smoothly in HFIP even at 20 °C (entry 5). Unfortunately, TFE was not effective in the reaction (entry 6). Conducting the reaction in HFIP at 60 °C accelerated the hydroamination, and alkenyl amine **2a** was consumed within 12 h, delivering pyrrolidine **3a** in 73% yield (entry 7) [19]. Olefin-isomerized product **4** was also obtained as a by-product. On these hydroaminations, enantioselectivity was not observed. In the chemistry of HFIP with Lewis or Brønsted acids, it is generally admitted that the true active species as a catalyst is HFIP activated with Lewis or Brønsted acids, and the activation mode is one of reasons for the absence of asymmetric induction on the hydroamination [18c]. Thus, we focused only on the catalytic ability of sulfonimide **1c** as a Brønsted acid in further investigations.

A comparison of catalytic efficiencies of several Brønsted acids with that of sulfonimide **1c** toward hydroamination is summarized in Table 2. An analogous catalytic hydroamination reaction using $Ca(NTf_2)_2$ in HFIP was reported by Gandon and Leboeuf [18c]. They found out that the reaction can be promoted by Tf_2NH. However, details regarding the Brønsted-acid-catalyzed hydroamination were not described. The hydroamination catalyzed by $TsOH\cdot H_2O$, Tf_2NH, TfOH, and **1c** afforded pyrrolidine **3a** in good chemical yield (entries 1–4). A small amount of 3-alkenyl amine **4a**, generated by acid-catalyzed olefin-isomerization, was also observed. When phosphoric acid **5** was used as the Brønsted acid, olefin-isomerized product, 3-alkenyl amine **4a**, was formed as the major product. This result indicated that in addition to the acidity of the Brønsted acid, the nucleophilicity of its conjugate base likewise affected the reaction outcome. The poor hydroamination result obtained with monosulfonimide **6** indicated the importance of adjacent sulfonimide groups for the high reactivity of sulfonimide **1** [20].

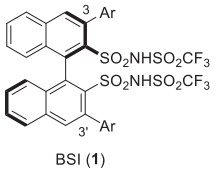
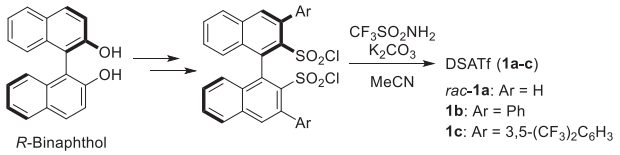


Fig. 1. BSI (**1**).



Scheme 1. Synthesis of BSI (**1**).

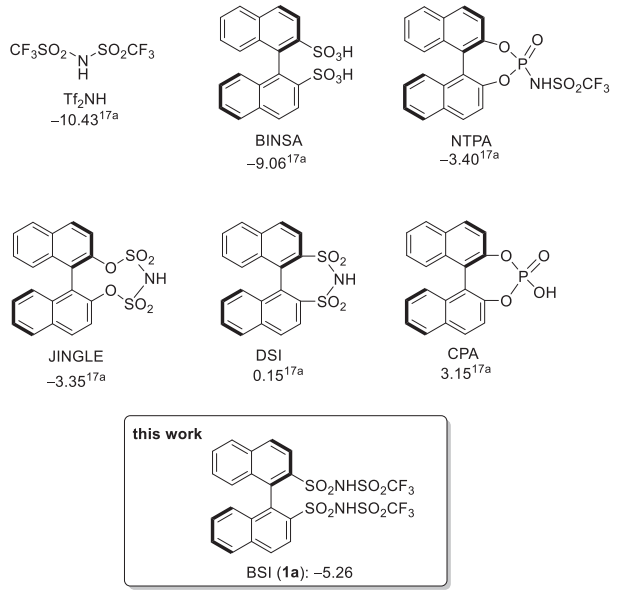
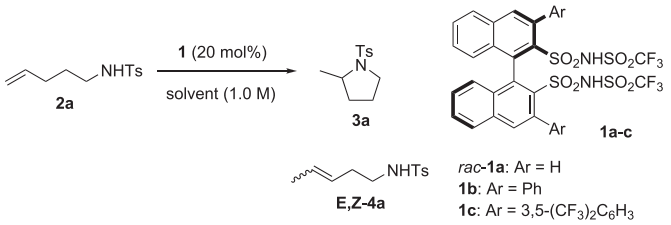


Fig. 2. Computationally predicted pK_a values of strong Brønsted acids in DMSO at the SMD/M06-2x/6−311++G(2df,2p)//B3LYP/6-31+G(d) level of theory.

Table 1
BSI catalyzed hydroamination of alkenyl amine **2a**.



entry	catalyst	conditions	yield (%)[a]	e.e. (%)[b]
1	*rac*-**1a**	DCM, 40 °C, 7 days	23	–
2	**1b**	DCM, 40 °C, 7 days	26	15
3	**1c**	DCM, 40 °C, 7 days	81	3
4	**1c**	benzene, 40 °C, 7 days	70	0
5	**1c**	HFIP, 20 °C, 4 days	82	N.D.
6	**1c**	TFE, 20 °C, 4 days then 40 °C, 3 days	25	0
7[c]	**1c**	HFIP, 60 °C, 12 h	73	N.D.

[a] Isolated yield.
[b] Determined by chiral stationary phase HPLC analysis.
[c] Alkene **4a**, which was generated from olefin-isomerization of **2a**, was also obtained: *E*-**4a**: 5.6% yield, *Z*-**4a**: 4.4% yield. Ts = *p*-$MeC_6H_4SO_2$. DCM = CH_2Cl_2. HFIP = $(CF_3)_2CHOH$. TFE = CF_3CH_2OH, N.D. = not determined.

Considering the time profile of the yield of pyrrolidine **3a** in the hydroamination reaction of **2a**, the order of Brønsted acid catalytic efficiency was $TsOH\cdot H_2O$, Tf_2NH > TfOH ≈ **1c** >> **6** (Fig. 3).

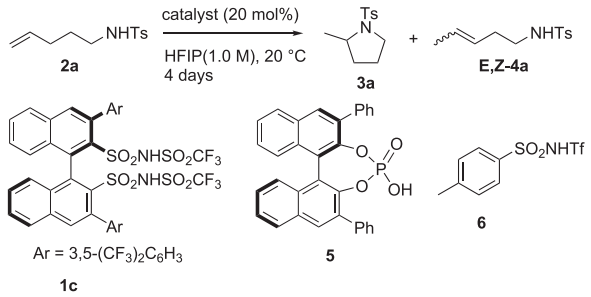
Next, the scope of **1c**-catalyzed hydroamination was examined (Table 3). Based on the results listed in Table 1, hydroamination of alkenyl amines **2** was performed at 60 °C. The introduction of a *gem*-methyl group on the alkenyl amine accelerated the reaction rate (entry 1). The hydroamination of alkenyl amine containing an internal olefin required a longer reaction time to consume the starting material than that of terminal olefin derivatives (entries 2 and 3). As olefin-isomerization of alkenyl amine was a competing reaction under hydroamination reaction conditions, pyrrolidine **3c** was generated as the major product in the case of alkenyl amine **2d** (entry 4) [21]. For phenyl-substituted alkenyl amines **2e** and **2f**, cyclization occurred at the benzylic position, wherein the most stable benzylic cation was generated, and pyrrolidine **3e** or piperidine **7f** was obtained, respectively (entries 5 and 6). However, when the reaction was performed at 20 °C with **2f**, the chemical yield of cyclization products **3f** and **7f** decreased and pyrrolidine **3f** was obtained as the major product. These data suggest that the reaction rate of the cyclization at 60 °C follows the order of 5-*exo* > terminal olefin-isomerization > internal olefin isomerization ≈ 5-*endo* > 6-*exo* (for **2a**-**d**) [22] and the benzylic cation intermediate is generated from **2e**,**f** as the stable cation intermediate at that temperature.

Finally, the scope of hydroalkoxylation catalyzed by **1c** was examined (Table 4). These reactions likewise proceeded via the most stable benzylic cation intermediate.

3. Conclusion

In conclusion, we have developed a novel Brønsted acid containing bis(trifluoromethanesulfonimide) (BSI) functionality. Computational prediction of the pK_a of BSI placed it in the category of strong Brønsted acids. The hydroamination reaction of alkenyl amine in HFIP was catalyzed by BSI with comparable efficiency to that of $TsOH\cdot H_2O$, Tf_2NH, and TfOH. However, enantioselectivity in the hydroamination was not observed, although BSI contained a chiral BINOL skeleton. A comparison of the catalytic efficiency of BSI with that of monosulfonimide **6** indicated the importance of adjacent sulfonimide groups for enhancing the acidity of BSI. BSI also catalyzed the hydroalkoxylation of alkenyl alcohols in HFIP with high efficiency. Advantages of BSI include its strong Brønsted acidity, reusability, and ease of handling than $TsOH\cdot H_2O$, Tf_2NH, and TfOH. Further studies aimed at developing a stereoselective reaction using BSI are currently underway in our laboratory.

Table 2
Comparison of catalytic efficiency of several Brønsted acids and **1c**.



Entry	catalyst	conv (%)[a]	yield (%)[b] 3a	*E*-4a	*Z*-4a
1	$TsOH\cdot H_2O$	96	89	3.9	3.2
2	Tf_2NH	94	88	3.6	2.3
3	TfOH	97	85	1	0.6
4	**1c**	86	82	2.5	1.8
5	**5**	81	7	61	6
6	**6**	48	33	9.4	3.3

[a] Determined by ^{1}H NMR measurement of the crude product using 1,3,5-trimethoxybenzene as an internal standard.
[b] Isolated yield.

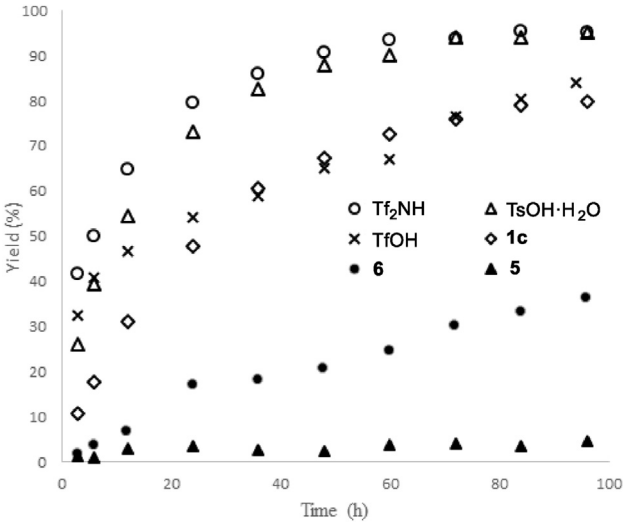


Fig. 3. Time profile of the chemical yield of pyrrolidine **3a** in the hydroamination of **2a**.

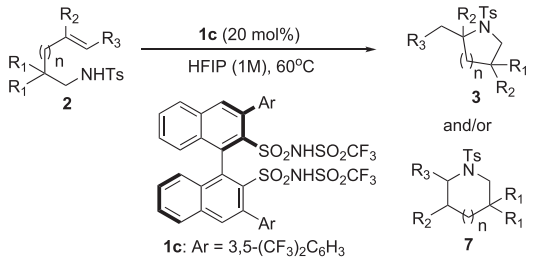
4. Experimental section

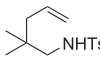
General Information. Internal references for ^{1}H NMR spectra were 0.0 ppm (Me_4Si) for $CDCl_3$ and CD_3OD (3.31 ppm). Chemical shifts for ^{13}C NMR spectra were referenced to $CDCl_3$ (77.0 ppm) and CD_3OD (49.0 ppm). Chemical shift for ^{19}F NMR spectra were reported on the basis on CF_3CO_2H (−76.0 ppm) as an external standard. High resolution mass spectral (HRMS) data were recorded with a LTQ Orbitrap trap mass spectrometer using electrospray ionization (ESI) method. Optical rotations were measured on a digital polarimeter with a 0.1 dm cell at room temperature. All reactions involving air- and moisture-sensitive reagents were carried out under N_2. All reactions were monitored by analytical thin-layer chromatography (TLC), which was visualized by ultraviolet light (254 nm).

Typical procedure for preparation of BSI. According to the literature procedure, the corresponding sulfonyl chloride was prepared by *N*-chlorosuccinimide (NCS) and the corresponding thiocarbamoyl derivative (for **1a**) [8c] or thionyl chloride and the corresponding sulfuric acid derivative (for **1b** and **1c**) [8b]. A mixture of the corresponding sulfonyl chloride (0.27 mmol), trifluoromethanesulfonamide (1.0 mmol), and K_2CO_3 (1.17 mmol) in MeCN (1.3 mL) was stirred at 70 °C for 24 h. The reaction mixture was quenched with 1 M HCl, and extracted by EtOAc. The organic layer was washed with H_2O and brine, dried over Na_2SO_4, and evaporated. The crude product was purified by column chromatography on silica gel, dissolved in CH_2Cl_2 and washed with 6 M HCl. Removing the solvent in vacuo yielded the desired product. BSI was dried in vacuo at 50 °C for 3 h before using.

BSI-1a. Purified by column chromatography (EtOAc/hexane = 20:1), 93% yield. White solid. m. p. 186–189 °C. $[\alpha]^D_{23}$ −35.7 (*c* 1.25, MeOH). IR (KBr) *ν* 391, 3250, 1638, 1321, 1192 cm^{-1}. ^{1}H NMR (500 MHz, CD_3OD) δ 8.30 (*J* = 8.7 Hz, 2 H), 8.09

Table 3
Scope of hydroamination catalyzed by **1c**.



entry	substrate	time	product[a]	
1	 **2b**	3 h	 **3b**: 92%	
2	 *E*-**2c**	24 h	 **3c**: 91%	
3	 *Z*-**2c**	96 h	 **3c**: 83%	 **7c**: 2%
4[b]	 **2d**	7 h	 **3c**: 50%	 **7c**: 14%
5[c]	 **2e**	9 h	 **3e**: 85%	
6[d]	 **2f**	1 h	 **3f**: 0%	 **7f**: 61%

[a] Isolated yield.
[b] A mixture of *E*− and *Z*-*N*-toluenesulfonyl 4-hexen-1-amine was also obtained in 8% yield.
[c] A mixture of *E*− and Z-isomer (*E*:*Z* = 5.3:1) was used as the substrate.
[d] When the reaction was carried out at 20 °C for 4 h, a mixture of pyrrolidine derivative and piperidine derivative was obtained (pyrrolidine **3f**: 20% yield, piperidine **7f**: 5% yield).

(d, *J* = 7.6 Hz, 2 H), 7.95 (d, *J* = 8.7 Hz, 2 H), 7.51 (t, *J* = 7.6 Hz, 2 H), 7.23 (t, *J* = 7.6 Hz, 2 H), 7.02 (d, *J* = 7.6 Hz, 2 H). ^{13}C NMR (125 MHz,CD_3OD) δ 140.5, 135.2, 134.7, 133.7, 129.1, 129.0, 128.3, 128.1, 127.4, 124.9, 120.8 (q, *J* = 320 Hz). ^{19}F NMR (470 MHz, CD_3OD) δ −79.65. HRMS (APCl$^+$) *m*/*z* calcd for $C_{22}H_{14}O_8N_2F_6NaS_4$ [M+Na]$^+$ 698.94110, found 698.94294.

Sulfonyl chloride for BSI-1b. White solid. m. p. 177−180 °C, $[\alpha]^D_{23}$ 85.9 (*c* 1.07, $CHCl_3$), IR (KBr) *ν* 1379, 1181 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (s, 2 H), 7.98 (d, *J* = 7.7 Hz, 2 H), 7.71 (t, *J* = 7.7 Hz, 2 H), 7.64-7.60 (m, 4 H), 7.52-7.44 (m, 8 H), 7.20 (d, *J* = 7.7 Hz, 2 H). ^{13}C NMR (100 MHz,$CDCl_3$) δ 140.0, 139.0, 137.6, 137.2, 135.0, 134.4, 131.6, 131.0, 130.5, 130.1, 128.5, 128.3, 128.1 (x2), 127.5, 127.3. HRMS (ESI+) *m*/*z* calcd for $C_{32}H_{20}O_4Cl_2NaS_2$ [M+Na]$^+$ 625.00072, found 625.00720.

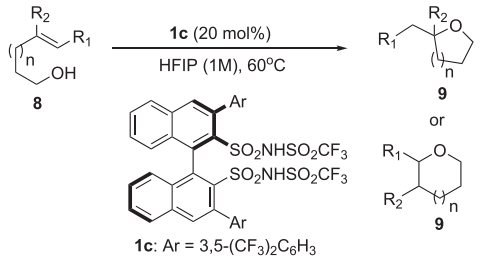
BSI-2b. Purified by column chromatography (EtOAc), 93% yield. White solid. m. p.104−105 °C. $[\alpha]^D_{23}$ 55.9 (*c* 1.26, $CHCl_3$). IR (KBr) *ν* 3434, 1620, 1308, 1190 cm^{-1}. ^{1}H NMR (400 MHz, CD_3OD) δ 7.86 (d, *J* = 8.0 Hz, 2 H), 7.78 (s, 2 H), 7.68 (d, *J* = 6.1 Hz, 4 H), 7.50 (t, *J* = 8.0 Hz, 2 H), 7.37-7.29 (m, 6 H), 7.23 (t, *J* = 8.0 Hz, 2 H), 7.15 (d, *J* = 8.0 Hz, 2 H). ^{13}C NMR (100 MHz, CD_3OD) δ 143.2, 139.7, 139.3, 138.9, 134.8, 133.8, 133.7, 131.8 (x2), 130.2, 129.3, 128.3, 128.0 (x2), 127.7 (x2), 120.8 (q, *J* = 323 Hz). ^{19}F NMR (376 MHz, CD_3OD) δ −79.15. HRMS (ESI−) *m*/*z* calcd for [M-2H + Na]$^{2-}$ $C_{34}H_{20}O_8N_2F_6NaS_4$ 848.99099, Found 848.99127.

BSI-3a. Purified by column chromatography (CH_2Cl_2/MeOH = 6:1), 83% yield. White solid. m. p.141−143 °C. $[\alpha]^D_{23}$ 48.5 (*c* 1.27, $CHCl_3$). IR (KBr) *ν* 3468, 1621, 1311, 1280, 1185 cm^{-1}. ^{1}H NMR (400 MHz, CD_3OD) δ 8.25 (s, 4 H), 7.96 (d, *J* = 8.0 Hz, 2 H), 7.91 (s, 2 H), 7.88 (s, 2 H), 7.58 (t, *J* = 8.0 Hz, 2 H), 7.35 (t, *J* = 8.0 Hz, 2 H), 7.13 (d, *J* = 8.0 Hz, 2 H). ^{13}C NMR (100 MHz, CD_3OD) δ 146.0, 139.4, 138.3, 136.6, 134.5, 134.2, 133.5, 132.8, 132.0, 131.4, 130.7, 130.0, 129.4, 128.5, 126.6, 125.2 (q, *J* = 273 Hz), 121.4, 121.0 (q, *J* = 320 Hz). ^{19}F NMR (376 MHz, CD_3OD) δ −62.1, −78.3. HRMS (ESI−) *m*/*z* calcd for $C_{38}H_{16}O_8N_2F_{18}S_4$ [M − 2H]$^{2-}$ 548.97565, found 548.97662.

The following compounds (**6** [23], **2a** [24], **2b** [25], **2c** [26], **2d** [24], **2e** [27], **8b** [28], **8c**[29]) were prepared according to the known procedures.

(4*E*)-Methyl-N-(5-phenylpent-4-en-1-yl) benzenesulfonamide (2f). A mixture of **2a** (51.0 mg, 0.23 mmol), Hoveyda-Grubbs catalyst 2nd generation (20.0 mg, 24.3 μmol), CH_2Cl_2 (4.0 mL) and styrene (90 μl, 0.78 mmol) was refluxed for 15 h [30]. The reaction mixture was evaporated to obtain the crude product. The crude

Table 4
Scope of hydroalkoxylation catalyzed by **1c**.



entry	substrate	time	product[a]
1	 **8a**	1 h	 **9a**: 78%
2[b]	 **8b**	4 h	 **9b**: 47%
3[c]	 **8c**	4 h	 **9c**: 62 %

[a] Isolated yield.
[b] A mixture of *E*– and *Z*-isomer (*E*:*Z* = 5.3:1) was used as the substrate.
[c] A mixture of *E*– and *Z*-isomer (*E*:*Z* = 22:1) was used as the substrate.

product was purified by column chromatography on silica gel (CH_2Cl_2) to give **2f** (36.6 mg, 51%) as a white solid. The spectral data of the purified product **2f** are in the agreement with the published data [31].

4-Phenylpent-4-en-1-ol (8a). 3-Phenyl-3-butenyl-1-cyanide was prepared according to known procedure [32]. Diisobutylaluminum hydride (DIBAL-H) (Ca. 1.0 M in hexane, 2.4 mL, 2.4 mmol) was added dropwise to 3-phenyl-3-butenyl-1-cyanide (240 mg, 1.5 mmol) in CH_2Cl_2 (4.4 mL) at −78 °C. After the reaction mixture was stirred at the temperature for 2 h, the mixture was quenched by sat. NH_4Cl at −78 °C. The reaction mixture was extracted with EtOAc, dried over Na_2SO_4, filtered, and concentrated in vacuo. $NaBH_4$ (66.0 mg, 1.7 mmol) was added slowly to the obtained crude product in MeOH (4.4 mL) at r. t., and the reaction mixture was stirred overnight. The mixture was quenched by sat. NH_4Cl, extracted with EtOAc, dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified by column chromatography (SiO_2, EtOAc/hexane = 15:1) to give **8a** (50 mg, 20% for 2 steps) as a colorless oil. The spectral data of the purified product **8a** are in the agreement with the published data [33].

Typical procedure for hydrofunctionalization. Alkenylamine 4-methyl-*N*-(pent-4-en-1-yl)benzenesulfonamide **2a** (41.0 mg, 0.17 mmol) was charged in a crew-cap vial equipped with a stir bar. A solution of BSI **1c** (37.7 mg, 34 μmol) in HFIP (0.17 mL) was added, and the tube was sealed. The reaction mixture was stirred at 60 °C and the progress of the reaction was monitored by thin layer chromatography. After the starting material was consumed, the reaction was quenched with solid $NaHCO_3$ and filtered. The filtrate was evaporated, and the crude product was purified by column chromatography (SiO_2, EtOAc/hexane = 15:1) to give hydrofunctionalization product **3a** (30 mg, 73%). The spectral data of the following products (**3a** [2a], **3b** [34], **3c** [35], **3e** [2a], **3f** [36], **7a** [37], **7c** [38], **7e** [2a], **9a** [39], **9b** [40], **9c**[41]) are in the agreement with the published data. Compounds **3c** and **7c** were obtained as a mixture in Table 3, entries 3 and 4.

Computational methods. The pK_a value of sulfonimide **1a** in DMSO has been predicted by the computational study using the direct method following X. Li, and J.-P. Cheng's method [18].

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.

5. Acknowledgements

MS, and optical rotation measurements were made at the Natural Science Center for Basic Research and Development (N-BARD), Hiroshima University.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.tet.2021.132037.

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