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NIS-Mediated intermolecular hydroamination of allenamides with imidazole heterocycles: a facile protocol for the synthesis of allylic *N*,*N*-acetals†

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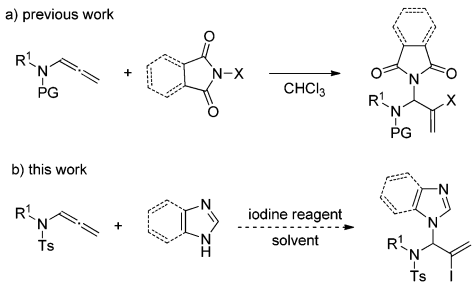
Allylic *N*,*N*-acetals are important intermediates in the synthesis of biologically active heterocycles and natural products. Herein, we report a facile protocol for the synthesis of this compound through *N*-iodosuccinimide-mediated hydroamination of allenamides by imidazole heterocycles. The reaction is regioselective, fast, and tolerant of a broad scope of imidazole and benzimidazole derivatives. The key intermediate is a conjugated sulfimide ion species that undergoes nucleophilic attack by imidazole to form the 1,2-adduct. Mixtures of N^1- and N^3-substituted isomers were obtained using asymmetrically substituted imidazoles. However, the 1,4-adduct was obtained using a tri-substituted imidazole. The efficiency of the gram-scale reaction suggests the potential industrial application of this synthetic method.

Introduction

The regioselective functionalization of carbon–carbon double bonds has enormous potential in organic synthesis.[1] Among compounds with C=C bonds, allenamides have recently proven to be important synthetic intermediates that undergo diverse, interesting transformations.[2] For instance, the hydroamination of allenamides is a straightforward conversion to form allylic *N*,*N*-acetals, which are key intermediates in the synthesis of biologically active heterocycles and natural products.[3] Broggini and co-workers reported an Au(III)-catalysed intramolecular hydroamination[4] and Pd-catalysed intramolecular carboamination[5] of allenamides to give allylic-substituted imidazolidine, 4-quinazolinone, and indoloimidazole derivatives. These reactions proceed through the coordination of the transition metal complex to the allenyl framework to afford vinyl-gold or palladium π-allyl intermediates. Although effective, these precious rare earth metals are expensive and scarce; thus, there remains much interest in developing more sustainable and greener protocols to synthesize allylic *N*,*N*-acetals.

Reactions with iodine electrophiles have been known for a long time.[6] The reaction with C=C bonds leads to a new stereogenic centre and that with C≡C bonds leads to functionalised alkenes. However, the activation of allenamides by an iodine electrophile still poses challenges with respect to regioselectivity. Only a few elegant examples of intramolecular cyclization involving allenamides have been reported to date.[7] At present, the key issue is that iodine-mediated hydroamination of allenamides to produce allylic *N*,*N*-acetals has not been reported except for one case described in our previous report.[8]

Imidazole derivatives have exhibited considerable biological activities such as antiinflammatory, antifungal, antiallergic, antileishmanial, and analgesic activities.[9] Notably, they are also useful precursors to N-heterocyclic carbenes, which serve as powerful ligands in various transition metal complexes.[10] Furthermore, chiral imidazole derivatives have been proven to be excellent organocatalysts in enantioselective kinetic resolutions.[11] Our previous studies on allenamides showed that allylic *N*,*N*-acetals can be obtained through regioselective 1,2-addition of *N*-haloimides, which serve as both electrophile and nucleophile in the reaction, to allenamides (Scheme 1a);[12] however, the substrate specificity of the reaction limit its broader utility.[13] To follow up on these results, we envisioned that imidazole heterocycles would also be of particular interest as reactants in this



Scheme 1 Synthesis of allylic *N*,*N*-acetals.

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hydroamination method to synthesize allylic *N*,*N*-acetals (Scheme 1b).

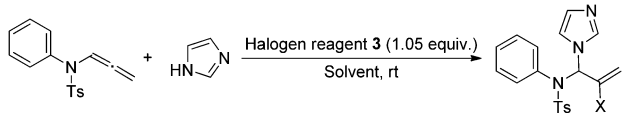
Results and discussion

Initial studies on the synthesis of heteroaromatic, allylic *N*,*N*-acetals were guided by our previous work on NIS-mediated iodofunctionalization of allenamides with indoles, pyrroles, and furans.[12g] Phenyl allenamide (**1a**) and imidazole (**2a**) were used to optimize the reaction conditions (Table 1). The first attempt using 1.05 equiv. NIS in CH_3CN provided the desired product, **4aa** as a single regioisomer in 5 minutes, with a yield of 96%, which is consistent with our previous report (entry 1).[8] The other halogen electrophiles were then evaluated. NCS, NBS and elemental iodine gave **4b** (16%), **4c** (26%) and **4aa** (50%), respectively. However, TCCA was not favoured for this transformation and gave the degradation product, 4-methyl-*N*-phenylbenzenesulfonamide, in 43% yield in 1 minute (entry 3). Further solvent optimization identified CH_3CN to be the best reaction medium (entries 6–12). The yield of **4aa** decreased to 73% when the reaction was carried out at 70 °C (entry 13).

After establishing the optimal reaction conditions for the present reaction, the reaction was conducted with various allenamide derivatives, as summarized in Table 2. 4-Me- or 4-MeO-substituted phenyl allenamides were suitable for the production of the allylic *N*,*N*-acetals **4ba**, and **4ca**, in 71% and 59% yield, respectively. The reaction of allenamides bearing F, Cl, and Br (*i.e.*, electron-withdrawing groups) at the *para* position of the aromatic ring resulted in the corresponding products, **4da** (97%), **4ea** (93%), and **4fa** (89%), respectively. Benzyl allenamide (**1g**) also provided the desired product, **4ga**, in 85% yield. Benzyl allenamides with different electron-donating and electron-withdrawing substituents, such as methyl, methoxy, fluoro, chloro, bromo, at the *para* position were all efficient in affording the desired products, **4ha–4la**, in 55–73% yields. Furthermore, the reactivity of the aliphatic-substituted allenamide, **1m**, was also investigated, and the allylic *N*,*N*-acetal, **4ma**, was obtained in 82% yield.

We then examined the NIS-mediated hydroamination of **1a** with different imidazole heterocycles (Table 3). Generally, the anticipated allylic *N*,*N*-acetals, **4ab–4al**, were obtained in modest to good yields. First, 2-substituted imidazoles, such as imidazole-2-carbaldehyde (**2b**) and 2-nitroimidazole (**2c**) were converted to the allylic *N*,*N*-acetals **4ab** (36%) and **4ac** (40%), respectively. In the case of asymmetrically substituted imidazoles, mixtures of N^1 and N^3-substituted isomers were obtained. Thus, complete regioselectivity was achieved for the conversion of 4-nitroimidazole (**2d**) to the N^1-substituted allylic *N*,*N*-acetal, **4ad** (65%).[14] In contrast, 4-iodoimidazole (**2e**) and imidazole-3-carbaldehyde (**2f**) showed low regioselectivity, yielding the N^1-substituted allylic *N*,*N*-acetals, **4ae** (16%) and **4af** (41%), as well as the N^3-substituted allylic *N*,*N*-acetals, **4ae′** (39%) and **4af′** (42%). The di-substituted imidazole (**2g**) also provided the product, **4ag**, in 44% yield. However, the tri-substituted imidazole, **2h**, only produced the 1,4-adduct, **5ah**, in 46% yield,

Table 1 Screening of optimal conditions[a]

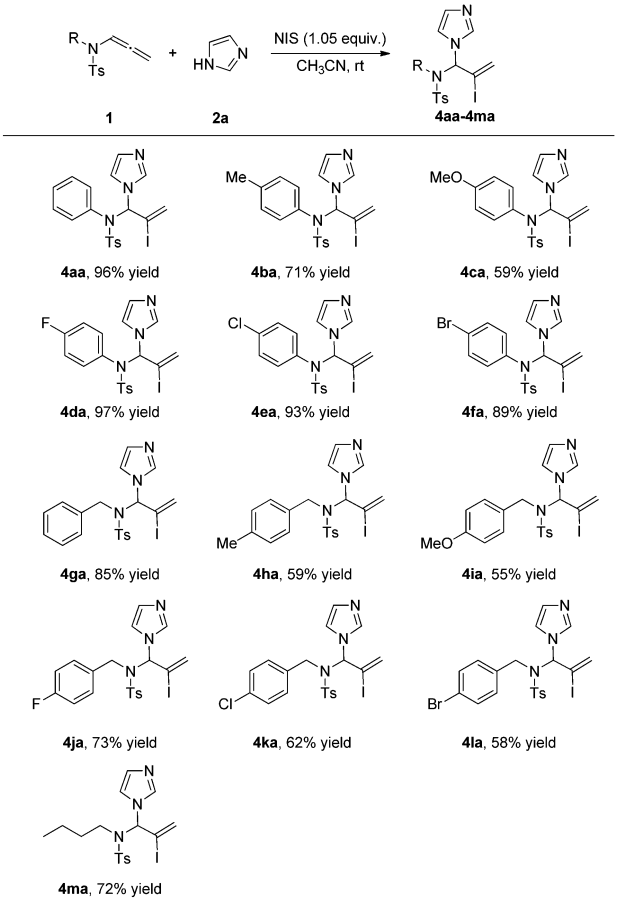


1a 2a 4

Entry	Halogen reagent **3**	Solvent	Yield of **4**[b] (%)
1	NIS	CH_3CN	**4aa** (96)
2	NCS	CH_3CN	**4b** (16)
3[c]	TCCA	CH_3CN	NP
4	NBS	CH_3CN	**4c** (26)
5[d]	I_2	CH_3CN	**4aa** (50)
6	NIS	DCM	**4aa** (86)
7	NIS	DCE	**4aa** (84)
8	NIS	$CHCl_3$	**4aa** (67)
9	NIS	Toluene	**4aa** (68)
10	NIS	Acetone	**4aa** (76)
11	NIS	DMF	**4aa** (42)
12	NIS	DMSO	**4aa** (25)
13[e]	NIS	CH_3CN	**4aa** (63)

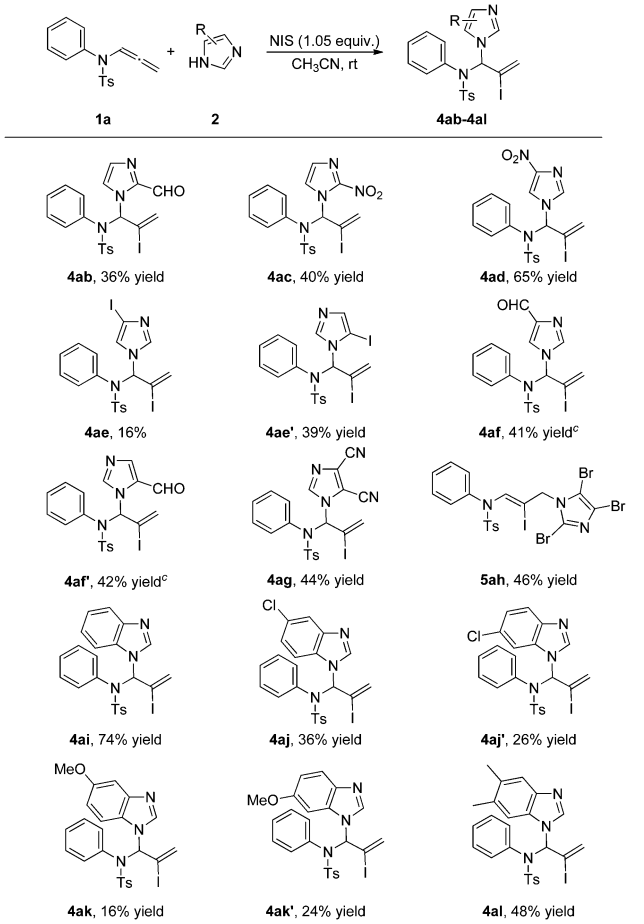
[a] Unless otherwise noted, all reactions were carried out at a 0.1 mmol of **1a**, 0.3 mmol of **2a** and 0.105 mmol of **3** in 2 mL solvent at rt within 5 min. [b] Isolated yield. [c] NP: no product. [d] **1a** was consumed within 15 min. [e] The reaction was carried out at 70 °C.

Table 2 Substrate scope of allenamides[a,b]



[a] Conditions: **1** (0.3 mmol), **2a** (0.6 mmol), NIS (0.315 mmol), CH_3CN (3 mL), rt, within 5 min. [b] Yield of isolated products.

Table 3 Substrate scope of imidazoles[a,b]



[a] Conditions: **1a** (0.3 mmol), **2** (0.6 mmol), NIS (0.315 mmol), CH_3CN (3 mL), rt, within 5 min. [b] Yield of isolated products. [c] Yield of ^{1}H NMR of mixture.

possibly because of steric hindrance. Remarkably, benzimidazole (**2i**) was also suitable for the preparation of the allylic *N*,*N*-acetal, **4ai**, in 73% yield. On the other hand, 5-chloro-1*H*-benzimidazole (**2j**) and 5-methoxy-1*H*-benzimidazole (**2k**) were converted to the N^1-substituted allylic *N*,*N*-acetals, **4aj** (36%) and **4ak** (16%), as well as the N^3-substituted allylic *N*,*N*-acetals, **4aj′** (26%) and **4ak′** (24%). The reaction was also efficient with di-substituted benzimidazole (**2l**), providing **4al** in 48% yield. Moreover, **4ak′** was a crystalline solid, and single-crystal X-ray analysis confirmed its structure (Fig. 1).[15]

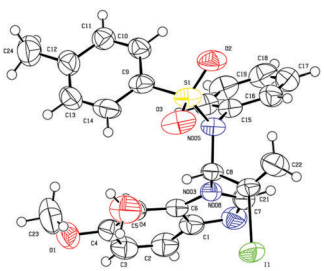
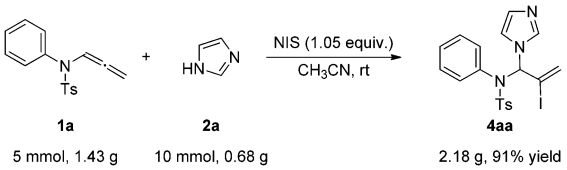
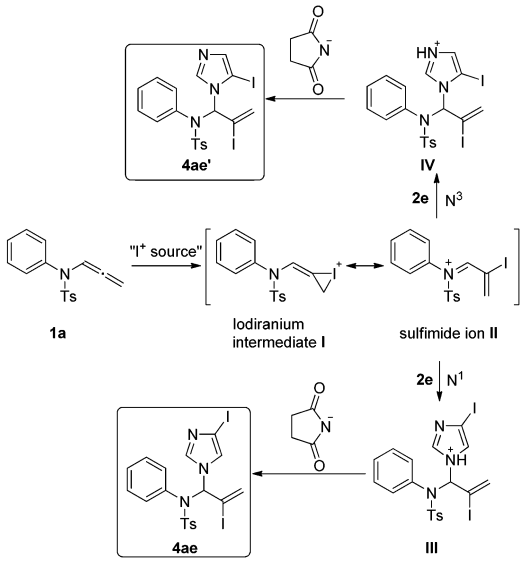


Fig. 1 X-ray structure of compound **4ak′**.



Scheme 2 Gram-scale reaction of allenamide (**1a**) with imidazole (**2a**).



Scheme 3 Proposed reaction pathway for hydroamination of allenamide (**1a**) with asymmetrically substituted imidazole (**2e**).

A scale-up of the reaction was subsequently carried out (Scheme 2). The reaction was proven to be scalable and practical because the gram-scale reaction was also efficiently performed. The reaction of **1a** (5 mmol, 1.43 g) and **2a** (10 mmol, 2 equiv.) gave the corresponding product **4aa** in 91% yield after 10 minutes under optimal reaction conditions.

On the basis of this and our previous study,[8] we propose a plausible reaction pathway, as shown in Scheme 3. The initial addition of NIS to **1a** is hypothesized to produce the key intermediate conjugated sulfimide ion **II**, *via* a decyclization reaction of iodiranium intermediate **I**. Then the N^1 or N^3 atom of **2e** as the nucleophile that promotes 1,2-addition to give intermediate **III** or **IV**. The proton of **III** or **IV** is trapped by the conjugate base of the imide to produce the allylic *N*,*N*-acetals, **4ae** and **4ae′**.

Experimental

General information

All reactions were conducted under open air at room temperature. ^{1}H NMR and ^{13}C NMR spectra were obtained with an Agilent Technologies 400 spectrometer in $CDCl_3$ with TMS as an internal standard. Chemical shifts (δ) are reported in ppm, and coupling constants (J) are in hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet,

d = doublet, t = triplet, q = quartet, m = multiplet, and br = broad. HRMS was performed using a Bruker Daltonics Bio TOF mass spectrometer. Melting points were determined from the solids obtained from column chromatography using a WRS-1B digital melting point instrument. All reactions were monitored by TLC. Flash column chromatography was carried out using 300–400 mesh silica gel at medium pressure. Commercial reagents were used as supplied or were purified by standard techniques where necessary. Allenamides **1a–1m** were prepared according to the reported method.[16]

General procedure for synthesis of compound allylic *N*,*N*-acetal 4aa

To a suspension of **1a** (0.3 mmol), **2a** (0.6 mmol) in CH_3CN (3 mL) was added **3a** (0.315 mmol) in one portion. Then the reaction mixture was stirred at room temperature until complete consumption of the starting material as monitored by TLC. The concentration of the reaction mixture *in vacuo* followed by purification through flash chromatography on a silica gel column (hexane/EtOAc = 1/1 as the eluent) afforded **4aa** (138 mg, 96% yield) as a yellow solid.

***N*-(1-(1*H*-Imidazol-1-yl)-2-iodoallyl)-4-methyl-*N*-phenylbenzenesulfonamide (4aa).** Purified by flash column chromatography (hexane/EtOAc = 1/1) in 96% yield (138 mg, 0.288 mmol) as a yellow solid. M.p. 86–87 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, J = 8.1 Hz, 2H), 7.33 (d, J = 9.1 Hz, 2H), 7.24–7.19 (m, 4H), 6.98 (s, 1H), 6.93 (s, 1H), 6.77 (d, J = 8.7 Hz, 2H), 6.74 (s, 1H), 6.65 (s, 1H), 6.24 (s, 1H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.49, 137.23, 135.57, 134.13, 131.96, 131.89, 129.67, 129.57, 129.27, 129.08, 127.78, 118.98, 102.82, 76.28, 21.58. HRMS (ESI) m/z calcd for $C_{19}H_{19}IN_3O_2S$ $[M + H]^+$ 480.0237; found, 480.0234.

***N*-(2-Chloro-1-(1*H*-imidazol-1-yl)allyl)-4-methyl-*N*-phenylbenzenesulfonamide (4b).** Purified by flash column chromatography (hexane/EtOAc = 2/1) in 16% yield (18.6 mg, 0.048 mmol) as a white solid. M.p. 71–72 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48–7.45 (m, 3H), 7.36 (t, J = 7.4 Hz, 1H), 7.26–7.21 (m, 4H), 7.08 (s, 1H), 6.98 (s, 1H), 6.85 (d, J = 7.7 Hz, 2H), 6.74 (s, 1H), 5.64 (s, 1H), 5.61 (s, 1H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.41, 137.16, 135.74, 135.67, 133.92, 132.08, 129.78, 129.52, 129.35, 129.14, 127.80, 119.26, 118.79, 72.66, 21.59. HRMS (ESI) m/z calcd for $C_{19}H_{19}ClN_3O_2S$ $[M + H]^+$ 388.0881; found, 388.0883.

***N*-(1-(1*H*-Imidazol-1-yl)-2-iodoallyl)-4-methyl-*N*-phenylbenzenesulfonamide (4c).** Purified by flash column chromatography (hexane/EtOAc = 1/1) in 26% yield (33.7 mg, 0.078 mmol) as a white solid. M.p. 64–65 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J = 8.3 Hz, 2H), 7.42 (s, 1H), 7.35 (t, J = 7.4 Hz, 1H), 7.23 (t, J = 7.9 Hz, 4H), 7.08 (s, 1H), 6.97 (s, 1H), 6.84 (d, J = 7.4 Hz, 2H), 6.72 (s, 1H), 6.13 (dd, J = 3.0, 1.7 Hz, 1H), 5.91 (dd, J = 3.0, 1.5 Hz, 1H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.43, 137.12, 135.59, 133.95, 132.00, 129.80, 129.56, 129.16, 128.73, 127.83, 126.28, 123.74, 118.93, 74.00, 21.61. HRMS (ESI) m/z calcd for $C_{19}H_{19}BrN_3O_2S$ $[M + H]^+$ 432.0376; found, 432.0379.

***N*-(1-(1*H*-Imidazol-1-yl)-2-iodoallyl)-4-methyl-*N*-(*p*-tolyl)benzenesulfonamide (4ba).** Purified by flash column chromatography (hexane/EtOAc = 1/1) in 71% yield (105 mg, 0.213 mmol) as a yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, J = 8.1 Hz, 2H), 7.37 (s, 1H), 7.24 (d, J = 8.1 Hz, 2H), 7.00 (d, J = 8.2 Hz, 2H), 6.97 (d, J = 7.3 Hz, 2H), 6.75 (s, 1H), 6.69 (s, 1H), 6.64 (d, J = 8.1 Hz, 2H), 6.23 (s, 1H), 2.42 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.45, 140.00, 137.12, 135.66, 132.07, 131.60, 131.24, 129.80, 129.58, 128.84, 127.82, 119.13, 102.76, 76.36, 21.61, 21.15. HRMS (ESI) m/z calcd for $C_{20}H_{21}IN_3O_2S$ $[M + H]^+$ 494.0394; found, 494.0391.

***N*-(1-(1*H*-Imidazol-1-yl)-2-iodoallyl)-*N*-(4-methoxyphenyl)-4-methylbenzenesulfonamide (4ca).** Purified by flash column chromatography (hexane/EtOAc = 1/1) in 59% yield (90.1 mg, 0.177 mmol) as a yellow solid. M.p. 103–104 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, J = 8.2 Hz, 2H), 7.23 (s, 1H), 7.11 (d, J = 8.1 Hz, 2H), 6.87 (s, 1H), 6.82 (s, 1H), 6.61 (s, 1H), 6.59–6.53 (m, 5H), 6.11 (s, 1H), 3.64 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.15, 144.35, 137.16, 135.53, 133.09, 131.85, 129.50, 129.12, 127.75, 125.99, 118.97, 114.13, 102.99, 76.11, 55.29, 21.54. HRMS (ESI) m/z calcd for $C_{20}H_{21}IN_3O_3S$ $[M + H]^+$ 510.0343; found, 510.0349.

***N*-(1-(1*H*-Imidazol-1-yl)-2-iodoallyl)-*N*-(4-fluorophenyl)-4-methylbenzenesulfonamide (4da).** Purified by flash column chromatography (hexane/EtOAc = 1/1) in 97% yield (144.7 mg, 0.291 mmol) as a yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, J = 8.3 Hz, 2H), 7.39 (s, 1H), 7.25 (d, J = 8.0 Hz, 2H), 7.00 (s, 1H), 6.95 (s, 1H), 6.91 (d, J = 8.1 Hz, 1H), 6.89 (d, J = 8.1 Hz, 1H), 6.77–6.73 (m, 2H), 6.71 (dd, J = 2.6, 1.8 Hz, 1H), 6.67 (s, 1H), 6.25 (dd, J = 2.6, 1.6 Hz, 1H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.89 (d, J = 250.2 Hz), 144.76, 137.08, 135.17, 133.86 (d, J = 8.9 Hz), 132.12, 129.78 (d, J = 3.2 Hz), 129.67, 129.11, 127.76, 118.90, 116.15 (d, J = 22.6 Hz), 102.51, 76.16, 21.56. HRMS (ESI) m/z calcd for $C_{19}H_{18}FIN_3O_2S$ $[M + H]^+$ 498.0143; found, 498.0142.

***N*-(1-(1*H*-Imidazol-1-yl)-2-iodoallyl)-*N*-(4-chlorophenyl)-4-methylbenzenesulfonamide (4ea).** Purified by flash column chromatography (hexane/EtOAc = 1/1) in 93% yield (143.2 mg, 0.279 mmol) as a yellow solid. M.p. 95–96 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, J = 8.1 Hz, 2H), 7.42 (s, 1H), 7.26 (d, J = 9.4 Hz, 2H), 7.19 (d, J = 8.5 Hz, 2H), 6.99 (d, J = 8.5 Hz, 2H), 6.73–6.69 (m, 4H), 6.24 (s, 1H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.84, 137.07, 136.06, 135.20, 133.22, 132.53, 132.28, 129.74, 129.40, 129.18, 127.81, 118.98, 102.39, 76.23, 21.62. HRMS (ESI) m/z calcd for $C_{19}H_{18}ClIN_3O_2S$ $[M + H]^+$ 513.9844; found, 513.9847.

***N*-(1-(1*H*-Imidazol-1-yl)-2-iodoallyl)-*N*-(4-bromophenyl)-4-methylbenzenesulfonamide (4fa).** Purified by flash column chromatography (hexane/EtOAc = 1/1) in 89% yield (148.9 mg, 0.267 mmol) as a yellow solid. M.p. 116–117 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, J = 8.2 Hz, 2H), 7.38 (s, 1H), 7.35 (d, J = 8.7 Hz, 2H), 7.26 (d, J = 8.1 Hz, 2H), 6.98 (d, J = 7.4 Hz, 2H), 6.69 (s, 1H), 6.67 (s, 1H), 6.64 (d, J = 8.6 Hz, 2H), 6.24 (s, 1H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.82, 137.13, 135.21, 133.49, 133.09, 132.40, 132.18, 129.73, 129.40, 127.78, 124.30, 118.90, 102.42, 76.13, 21.62. HRMS (ESI) m/z calcd for $C_{19}H_{18}BrIN_3O_2S$ $[M + H]^+$ 557.9342; found, 557.9343.

***N*-(1-(1*H*-Imidazol-1-yl)-2-iodoallyl)-*N*-benzyl-4-methylbenzenesulfonamide (4ga).** Purified by flash column chromatography (hexane/EtOAc = 2/1) in 85% yield (125.8 mg, 0.255 mmol) as a yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 8.2 Hz, 2H),

7.26 (s, 1H), 7.16–7.10 (m, 5H), 6.93 (d, J = 6.9 Hz, 2H), 6.91 (s, 1H), 6.63 (s, 1H), 6.48 (s, 1H), 6.27 (s, 1H), 6.09 (s, 1H), 4.38 (d, J = 15.7 Hz, 1H), 4.29 (d, J = 15.7 Hz, 1H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.31, 137.13, 136.26, 135.03, 132.37, 129.73, 129.60, 128.75, 128.47, 128.07, 127.34, 118.65, 101.07, 76.37, 49.52, 21.55. HRMS (ESI) m/z calcd for $C_{20}H_{20}IN_3O_2S$ $[M + H]^+$ 494.0394; found, 494.0390.

***N*-(1-(1*H*-Imidazol-1-yl)-2-iodoallyl)-4-methyl-*N*-(4-methylbenzyl)benzenesulfonamide (4ha).** Purified by flash column chromatography (hexane/EtOAc = 2/1) in 59% yield (89.8 mg, 0.177 mmol) as a yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, J = 8.2 Hz, 2H), 7.30 (s, 1H), 7.22 (d, J = 8.1 Hz, 2H), 7.00 (d, J = 8.1 Hz, 2H), 6.99 (s, 1H), 6.90 (d, J = 7.9 Hz, 2H), 6.70 (s, 1H), 6.51 (s, 1H), 6.34 (s, 1H), 6.16 (s, 1H), 4.41 (d, J = 15.5 Hz, 1H), 4.29 (d, J = 15.6 Hz, 1H), 2.42 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.23, 137.93, 137.19, 136.30, 132.38, 131.98, 129.68, 129.55, 129.14, 128.78, 127.36, 118.72, 101.09, 76.34, 49.34, 21.55, 21.07. HRMS (ESI) m/z calcd for $C_{21}H_{23}IN_3O_2S$ $[M + H]^+$ 508.0550; found, 508.0552.

***N*-(1-(1*H*-Imidazol-1-yl)-2-iodoallyl)-*N*-(4-methoxybenzyl)-4-methylbenzenesulfonamide (4ia).** Purified by flash column chromatography (hexane/EtOAc = 2/1) in 55% yield (86.4 mg, 0.165 mmol) as a yellow solid. M.p. 112–113 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 8.2 Hz, 2H), 7.27 (s, 1H), 7.15 (d, J = 8.1 Hz, 2H), 6.93 (s, 1H), 6.86 (d, J = 8.5 Hz, 2H), 6.66 (s, 2H), 6.65 (d, J = 8.4 Hz, 1H), 6.44 (s, 1H), 6.27 (s, 1H), 6.10 (s, 1H), 4.31 (d, J = 15.4 Hz, 1H), 4.21 (d, J = 15.5 Hz, 1H), 3.70 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.41, 144.22, 137.17, 136.38, 132.41, 130.32, 129.71, 129.49, 127.34, 126.96, 118.75, 113.83, 101.13, 77.36, 55.24, 49.04, 21.57. HRMS (ESI) m/z calcd for $C_{21}H_{23}IN_3O_3S$ $[M + H]^+$ 524.0499; found, 524.0498.

***N*-(1-(1*H*-Imidazol-1-yl)-2-iodoallyl)-*N*-(4-fluorobenzyl)-4-methylbenzenesulfonamide (4ja).** Purified by flash column chromatography (hexane/EtOAc = 1/1) in 73% yield (109.3 mg, 0.219 mmol) as a yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, J = 8.2 Hz, 2H), 7.39 (s, 1H), 7.23 (d, J = 8.2 Hz, 2H), 6.99–6.96 (m, 3H), 6.86 (t, J = 8.6 Hz, 2H), 6.73 (s, 1H), 6.60 (s, 1H), 6.31 (s, 1H), 6.17 (s, 1H), 4.39 (s, 2H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.34 (d, J = 245.9 Hz), 144.44, 136.97, 136.16, 132.36, 130.83 (d, J = 3.3 Hz), 130.48 (d, J = 8.1 Hz), 129.73, 129.63, 127.26, 118.51, 115.27 (d, J = 21.5 Hz), 101.00, 76.34, 48.62, 21.52. HRMS (ESI) m/z calcd for $C_{20}H_{20}FIN_3O_2S$ $[M + H]^+$ 512.0299; found512.0297.

***N*-(1-(1*H*-Imidazol-1-yl)-2-iodoallyl)-*N*-(4-chlorobenzyl)-4-methylbenzenesulfonamide (4ka).** Purified by flash column chromatography (hexane/EtOAc = 2/1) in 62% yield (95.8 mg, 0.186 mmol) as a yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 8.2 Hz, 2H), 7.37 (s, 1H), 7.16 (d, J = 8.1 Hz, 2H), 7.07 (d, J = 8.3 Hz, 2H), 6.93 (s, 1H), 6.86 (d, J = 8.3 Hz, 2H), 6.67 (s, 1H), 6.56 (s, 1H), 6.25 (s, 1H), 6.11 (s, 1H), 4.34 (d, J = 15.9 Hz, 1H), 4.29 (d, J = 15.9 Hz, 1H), 2.35 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.56, 136.93, 136.09, 133.96, 133.56, 132.45, 130.00, 129.78, 129.59, 128.53, 127.30, 118.51, 100.96, 76.39, 48.69, 21.57. HRMS (ESI) m/z calcd for $C_{20}H_{20}ClIN_3O_2S$ $[M + H]^+$ 528.0004; found, 528.0009.

***N*-(1-(1*H*-Imidazol-1-yl)-2-iodoallyl)-*N*-(4-bromobenzyl)-4-methylbenzenesulfonamide (4la).** Purified by flash column chromatography (hexane/EtOAc = 2/1) in 58% yield (97.3 mg, 0.174 mmol) as a white solid. M.p. 103–104 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, J = 8.2 Hz, 2H), 7.40 (s, 1H), 7.22 (d, J = 8.3 Hz, 2H), 7.16 (d, J = 8.1 Hz, 2H), 6.94 (s, 1H), 6.80 (d, J = 8.3 Hz, 2H), 6.68 (s, 1H), 6.57 (s, 1H), 6.25 (s, 1H), 6.11 (s, 1H), 4.32 (d, J = 16.1 Hz, 1H), 4.28 (d, J = 16.1 Hz, 1H), 2.35 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.59, 136.92, 136.09, 134.05, 132.50, 131.50, 130.33, 129.79, 129.50, 127.31, 122.13, 118.53, 100.93, 76.43, 48.76, 21.59. HRMS (ESI) m/z calcd for $C_{20}H_{20}BrIN_3O_2S$ $[M + H]^+$ 571.9499; found, 571.9495.

***N*-(1-(1*H*-Imidazol-1-yl)-2-iodoallyl)-*N*-butyl-4-methylbenzenesulfonamide (4ma).** Purified by flash column chromatography (hexane/EtOAc = 2/1) in 72% yield (99.2 mg, 0.216 mmol) as a yellow solid. M.p. 91–92 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 8.3 Hz, 2H), 7.39 (s, 1H), 7.22 (d, J = 8.2 Hz, 2H), 6.97 (s, 1H), 6.79 (s, 1H), 6.58 (s, 1H), 6.16–6.13 (m, 1H), 6.09–6.08 (m, 1H), 3.19–3.10 (m, 1H), 3.04–2.96 (m, 1H), 2.36 (s, 3H), 1.53–1.42 (m, 1H), 1.1–1.01 (m, 2H), 0.98–0.87 (m, 1H), 0.73 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.30, 136.67, 135.95, 131.58, 129.83, 129.68, 127.21, 118.21, 101.58, 76.06, 45.70, 31.79, 21.56, 20.24, 13.42. HRMS (ESI) m/z calcd for $C_{17}H_{23}IN_3O_2S$ $[M + H]^+$ 460.0550; found, 460.0555.

***N*-(1-(2-Formyl-1*H*-imidazol-1-yl)-2-iodoallyl)-4-methyl-*N*-phenylbenzenesulfonamide (4ab).** Purified by flash column chromatography (hexane/EtOAc = 3/1) in 36% yield (54.8 mg, 0.108 mmol) as a yellow solid. M.p. 103–104 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.75 (d, J = 0.9 Hz, 1H), 7.97 (s, 1H), 7.46 (d, J = 8.3 Hz, 2H), 7.26 (t, J = 7.4 Hz, 1H), 7.17–7.11 (m, 4H), 7.00 (d, J = 0.8 Hz, 1H), 6.89 (s, 1H), 6.84 (dd, J = 2.6, 1.7 Hz, 1H), 6.80 (d, J = 7.4 Hz, 2H), 6.17 (dd, J = 2.6, 1.4 Hz, 1H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.02, 144.34, 142.45, 135.15, 134.80, 132.09, 131.59, 131.29, 129.56, 129.28, 129.17, 128.38, 124.98, 103.58, 75.67, 21.59. HRMS (ESI) m/z calcd for $C_{20}H_{19}IN_3O_3S$ $[M + H]^+$ 508.0186; found, 508.0190.

***N*-(2-Iodo-1-(2-nitro-1*H*-imidazol-1-yl)allyl)-4-methyl-*N*-phenylbenzenesulfonamide (4ac).** Purified by flash column chromatography (hexane/EtOAc = 3/1) in 40% yield (62.9 mg, 0.120 mmol) as a white solid. M.p. 93–94 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.43 (d, J = 8.3 Hz, 2H), 7.31–7.27 (m, 1H), 7.18–7.16 (m, 4H), 6.96 (d, J = 1.2 Hz, 1H), 6.89 (d, J = 1.2 Hz, 1H), 6.85 (d, J = 7.4 Hz, 2H), 6.79 (dd, J = 2.8, 1.6 Hz, 1H), 6.19 (dd, J = 2.8, 1.2 Hz, 1H), 2.35 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.82, 134.68, 134.35, 132.53, 131.98, 129.87, 129.52, 129.37, 128.20, 127.73, 124.37, 101.79, 78.04, 21.60. HRMS (ESI) m/z calcd for $C_{19}H_{18}IN_4O_4S$ $[M + H]^+$ 525.0088; found, 525.0090.

***N*-(2-Iodo-1-(4-nitro-1*H*-imidazol-1-yl)allyl)-4-methyl-*N*-phenylbenzenesulfonamide (4ad).** Purified by flash column chromatography (hexane/EtOAc = 3/1) in 65% yield (102.2 mg, 0.195 mmol) as a yellow solid. M.p. 92–93 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (s, 1H), 7.46 (d, J = 8.1 Hz, 2H), 7.38 (s, 1H), 7.35 (d, J = 7.4 Hz, 1H), 7.26–7.20 (m, 4H), 6.96 (s, 1H), 6.83 (d, J = 7.7 Hz, 2H), 6.66 (s, 1H), 6.26 (s, 1H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.68, 145.26, 135.98, 134.98, 133.63, 131.83, 130.36, 129.84,

129.74, 129.63, 127.87, 118.81, 100.35, 77.39, 21.66. HRMS (ESI) *m*/*z* calcd for $C_{19}H_{18}IN_4O_4S$ $[M + H]^+$ 525.0088; found, 525.0085.

***N*-(2-Iodo-1-(4-iodo-1*H*-imidazol-1-yl)allyl)-4-methyl-*N*-phenylbenzenesulfonamide (4ae).** Purified by flash column chromatography (hexane/EtOAc = 4/1) in 16% yield (29.1 mg, 0.048 mmol) as a white solid. M.p. 77–78 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, J = 8.1 Hz, 2H), 7.37 (t, J = 7.4 Hz, 1H), 7.30–7.22 (m, 5H), 6.92 (s, 1H), 6.83 (d, J = 7.9 Hz, 2H), 6.76 (s, 1H), 6.68 (s, 1H), 6.23 (s, 1H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.75, 138.76, 135.43, 134.13, 132.65, 131.86, 129.93, 129.67, 129.27, 128.29, 127.83, 124.50, 101.57, 76.56, 21.64. HRMS (ESI) *m*/*z* calcd for $C_{19}H_{18}I_2N_3O_2S$ $(M + H)^+$ 605.9204; found, 605.9210.

***N*-(2-Iodo-1-(5-iodo-1*H*-imidazol-1-yl)allyl)-4-methyl-*N*-phenylbenzenesulfonamide (4ae′).** Purified by flash column chromatography (hexane/EtOAc = 2/1) in 39% yield (70.8 mg, 0.117 mmol) as a white solid. M.p. 81–82 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, J = 8.3 Hz, 2H), 7.28 (t, J = 7.4 Hz, 1H), 7.18–7.15 (m, 4H), 7.03 (s, 1H), 6.99 (s, 1H), 6.96–6.94 (m, 2H), 6.79 (d, J = 7.8 Hz, 2H), 6.32–6.29 (m, 1H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.45, 139.78, 136.73, 135.33, 134.04, 134.02, 132.11, 131.54, 129.83, 129.34, 129.29, 128.34, 103.93, 77.44, 21.64. HRMS (ESI) *m*/*z* calcd for $C_{19}H_{18}I_2N_3O_2S$ $(M + H)^+$ 605.9204; found, 605.9209.

***N*-(1-(4-Formyl-1*H*-imidazol-1-yl)-2-iodoallyl)-4-methyl-*N*-phenylbenzenesulfonamide (4af).** Purified by flash column chromatography (hexane/EtOAc = 4/1) in 41% yield (62.4 mg, 0.123 mmol) as a yellow solid. M.p. 66–67 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.74 (s, 1H), 7.44–7.38 (m, 3H), 7.33–7.27 (m, 2H), 7.20–7.15 (m, 4H), 6.94 (s, 1H), 6.74 (d, J = 7.8 Hz, 2H), 6.66 (s, 1H), 6.21 (s, 1H), 2.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.86, 144.96, 141.83, 138.64, 135.22, 133.83, 132.92, 131.86, 130.13, 129.75, 129.46, 127.83, 124.09, 101.32, 76.90, 21.65. HRMS (ESI) *m*/*z* calcd for $C_{20}H_{19}IN_3O_3S$ $[M + H]^+$ 508.0186; found, 508.0190.

***N*-(1-(5-Formyl-1*H*-imidazol-1-yl)-2-iodoallyl)-4-methyl-*N*-phenylbenzenesulfonamide (4af′).** Purified by flash column chromatography (hexane/EtOAc = 3/1) in 42% yield (64.0 mg, 0.126 mmol) as a white solid. M.p. 55–56 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.70 (s, 1H), 7.80 (s, 1H), 7.67 (s, 1H), 7.46 (d, J = 8.0 Hz, 3H), 7.27 (t, J = 7.4 Hz, 1H), 7.18–7.13 (m, 4H), 6.87 (s, 1H), 6.83 (d, J = 7.7 Hz, 2H), 6.19 (s, 1H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.23, 144.37, 143.71, 140.08, 135.27, 134.72, 132.08, 131.99, 129.76, 129.34, 129.27, 128.42, 127.20, 103.71, 75.78, 21.62. HRMS (ESI) *m*/*z* calcd for $C_{20}H_{19}IN_3O_3S$ $[M + H]^+$ 508.0186; found 508.0185.

***N*-(1-(4,5-Dicyano-1*H*-imidazol-1-yl)-2-iodoallyl)-4-methyl-*N*-phenylbenzenesulfonamide (4ag).** Purified by flash column chromatography (hexane/EtOAc = 3/1) in 44% yield (69.9 mg, 0.132 mmol) as a white solid. M.p. 88–89 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (s, 1H), 7.49 (d, J = 8.2 Hz, 2H), 7.43 (t, J = 7.4 Hz, 1H), 7.34–7.28 (m, 4H), 7.00 (d, J = 1.1 Hz, 1H), 6.93 (s, 1H), 6.90 (d, J = 7.7 Hz, 2H), 6.40 (d, J = 1.9 Hz, 1H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.55, 141.17, 134.79, 134.30, 133.68, 131.92, 130.57, 129.96, 129.83, 128.03, 123.53, 111.82, 111.10, 107.27, 99.67, 76.78, 21.75. HRMS (ESI) *m*/*z* calcd for $C_{21}H_{16}IN_5O_2SNa$ $[M + Na]^+$ 551.9962; found, 551.9963.

***(Z)*-*N*-(2-Iodo-3-(2,4,5-tribromo-1*H*-imidazol-1-yl)prop-1-en-1-yl)-4-methyl-*N*-phenylbenzenesulfonamide (5ah).** Purified by flash column chromatography (hexane/EtOAc = 4/1) in 46% yield (96.5 mg, 0.138 mmol) as a white solid. M.p. 97–98 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, J = 8.1 Hz, 2H), 7.29–7.28 (m, 3H), 7.25–7.23 (m, 2H), 7.04 (s, 1H), 7.02–7.00 (m, 2H), 4.87 (s, 2H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.85, 137.41, 135.43, 133.76, 129.71, 129.66, 128.95, 128.26, 127.82, 118.92, 117.52, 105.54, 84.26, 56.99, 21.65. HRMS (ESI) *m*/*z* calcd for $C_{19}H_{15}Br_3IN_3O_2SNa$ $[M + Na]^+$ 737.7352; found, 737.7351.

***N*-(1-(1*H*-Benzo[*d*]imidazol-1-yl)-2-iodoallyl)-4-methyl-*N*-phenylbenzenesulfonamide (4ai).** Purified by flash column chromatography (hexane/EtOAc = 2/1) in 74% yield (117.5 mg, 0.222 mmol) as a white solid. M.p. 91–92 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78–7.72 (m, 1H), 7.47 (d, J = 8.0 Hz, 2H), 7.41 (s, 1H), 7.39–7.35 (m, 1H), 7.33–7.22 (m, 4H), 7.17 (d, J = 7.9 Hz, 2H), 7.09 (t, J = 7.7 Hz, 2H), 7.05 (s, 1H), 6.63 (d, J = 7.6 Hz, 2H), 6.37 (s, 1H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.48, 142.98, 142.19, 135.49, 134.15, 132.98, 131.98, 131.79, 129.79, 129.52, 129.22, 127.83, 123.86, 123.06, 120.61, 110.01, 103.49, 74.80, 21.59. HRMS (ESI) *m*/*z* calcd for $C_{23}H_{21}IN_3O_2S$ $[M + H]^+$ 530.0394; found, 530.0398.

***N*-(1-(5-Chloro-1*H*-benzo[*d*]imidazol-1-yl)-2-iodoallyl)-4-methyl-*N*-phenylbenzenesulfonamide (4aj).** Purified by flash column chromatography (hexane/EtOAc = 4/1) in 36% yield (60.9 mg, 0.108 mmol) as a yellow solid. M.p. 80–81 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (s, 1H), 7.46 (d, J = 8.1 Hz, 2H), 7.43 (s, 1H), 7.28–7.18 (m, 6H), 7.10 (t, J = 7.6 Hz, 2H), 7.04 (s, 1H), 6.62 (d, J = 7.8 Hz, 2H), 6.38 (s, 1H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.66, 143.86, 143.41, 135.38, 134.05, 132.20, 131.71, 131.61, 129.91, 129.58, 129.31, 128.72, 127.80, 124.31, 120.46, 110.93, 102.98, 74.93, 21.59. HRMS (ESI) *m*/*z* calcd for $C_{23}H_{20}ClIN_3O_2S$ $[M + H]^+$ 564.0004; found, 564.0008.

***N*-(1-(6-Chloro-1*H*-benzo[*d*]imidazol-1-yl)-2-iodoallyl)-4-methyl-*N*-phenylbenzenesulfonamide (4aj′).** Purified by flash column chromatography (hexane/EtOAc = 3/1) in 26% yield (44 mg, 0.078 mmol) as a yellow solid. M.p. 97–98 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 8.6 Hz, 1H), 7.52 (d, J = 8.3 Hz, 2H), 7.39 (s, 1H), 7.29–7.23 (m, 4H), 7.17–7.15 (m, 2H), 7.11 (t, J = 7.9 Hz, 2H), 7.08 (s, 1H), 6.61 (d, J = 7.6 Hz, 2H), 6.44–6.41 (m, 1H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.83, 142.91, 141.57, 135.30, 134.05, 133.54, 132.33, 131.63, 129.94, 129.77, 129.74, 129.33, 127.80, 123.84, 121.46, 110.14, 102.91, 74.90, 21.68. HRMS (ESI) *m*/*z* calcd for $C_{23}H_{20}ClIN_3O_2S$ $[M + H]^+$ 564.0004; found, 564.0007.

***N*-(2-Iodo-1-(5-methoxy-1*H*-benzo[*d*]imidazol-1-yl)allyl)-4-methyl-*N*-phenylbenzenesulfonamide (4ak).** Purified by flash column chromatography (hexane/EtOAc = 2/1) in 16% yield (26.9 mg, 0.048 mmol) as a yellow solid. M.p. 70–71 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, J = 8.1 Hz, 2H), 7.31 (s, 1H), 7.20 (d, J = 7.5 Hz, 1H), 7.14 (d, J = 8.3 Hz, 5H), 7.05 (t, J = 7.7 Hz, 2H), 7.00 (s, 1H), 6.86 (dd, J = 8.8, 1.7 Hz, 1H), 6.58 (d, J = 7.7 Hz, 2H), 6.32 (s, 1H), 3.81 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.55, 144.46, 143.89, 142.44, 135.49, 134.13, 131.87, 131.78, 129.75, 129.51, 129.16, 127.84, 113.83, 110.45, 103.48, 102.60, 74.88, 55.70, 21.56. HRMS (ESI) *m*/*z* calcd for $C_{24}H_{23}IN_3O_3S$ $[M + H]^+$ 560.0499; found, 560.0500.

***N*-(2-Iodo-1-(6-methoxy-1*H*-benzo[*d*]imidazol-1-yl)allyl)-4-methyl-*N*-phenylbenzenesulfonamide (4ak′).** Purified by flash column

chromatography (hexane/EtOAc = 3/1) in 24% yield (40.3 mg, 0.072 mmol) as a white solid. M.p. 58–59 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 8.8 Hz, 1H), 7.42 (d, J = 8.3 Hz, 2H), 7.22 (s, 1H), 7.18 (d, J = 7.5 Hz, 1H), 7.12 (d, J = 8.4 Hz, 3H), 7.03 (t, J = 7.8 Hz, 2H), 7.00–6.97 (m, 1H), 6.85 (dd, J = 8.8, 2.3 Hz, 1H), 6.75 (d, J = 2.1 Hz, 1H), 6.57 (d, J = 7.7 Hz, 2H), 6.33–6.29 (m, 1H), 3.78 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.36, 144.50, 141.18, 137.28, 135.55, 134.11, 133.67, 131.84, 129.79, 129.56, 129.20, 127.80, 121.04, 112.48, 103.50, 93.54, 74.75, 55.81, 21.59. HRMS (ESI) m/z calcd for $C_{24}H_{23}IN_3O_3S$ $[M + H]^+$ 560.0499; found, 560.0504.

***N*-(1-(5,6-Dimethyl-1*H*-benzo[d]imidazol-1-yl)-2-iodoallyl)-4-methyl-*N*-phenylbenzenesulfonamide (4al).** Purified by flash column chromatography (hexane/EtOAc = 3/1) in 48% yield (80.3 mg, 0.144 mmol) as a white solid. M.p. 61–62 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, J = 8.0 Hz, 2H), 7.46 (s, 1H), 7.24–7.16 (m, 4H), 7.13 (s, 1H), 7.05 (d, J = 8.2 Hz, 3H), 7.02 (s, 1H), 6.58 (d, J = 7.7 Hz, 2H), 6.34 (s, 1H), 2.36 (s, 3H), 2.33 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.42, 141.48, 141.25, 135.60, 134.09, 133.12, 131.99, 131.77, 131.67, 131.49, 129.73, 129.53, 129.17, 127.89, 120.60, 109.89, 103.82, 74.54, 21.62, 20.55, 20.27. HRMS (ESI) m/z calcd for $C_{25}H_{25}IN_3O_2S$ $[M + H]^+$ 558.0707; found, 558.0705.

Conclusions

In conclusion, we developed a facile protocol for the synthesis of allylic *N*,*N*-acetals through NIS-mediated hydroamination of allenamides by imidazole derivatives. Regioselective 1,2-addition and broad substrate specificity were achieved, thereby overcoming the previous limitations of allenamide activation by an iodine electrophile. Imidazole acts as the nucleophile, which attacks the conjugated sulfimide ion intermediate to yield the 1,2-adduct. This green synthetic method provides an alternative to the corresponding transition-metal-catalysed reaction and shows promise for large-scale application. The potential utilization and extension of this interesting synthetic method are currently underway.

Conflicts of interest

There are no conflicts to declare.

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14 The structure of **4ad** was confirmed by the NOE spectrum, see ESI†.

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