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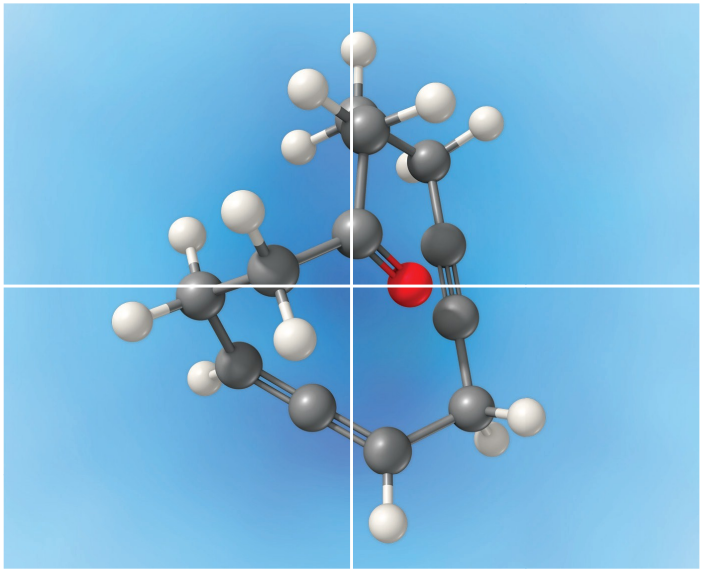

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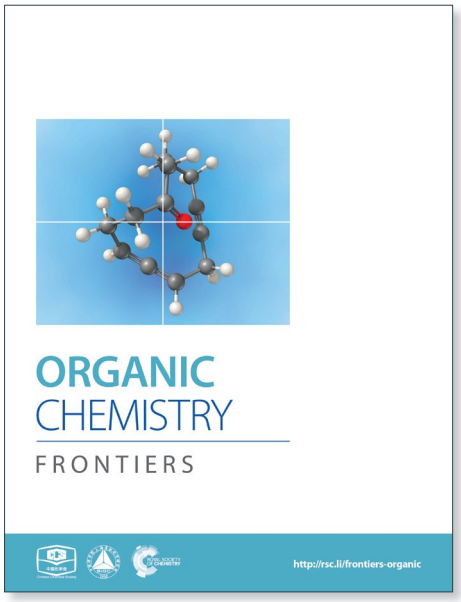


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Organic Chemistry Frontiers

ARTICLE

# Copper-Catalyzed Multi-Component Synthesis of Acrylamidines and Benzoimidiazoles

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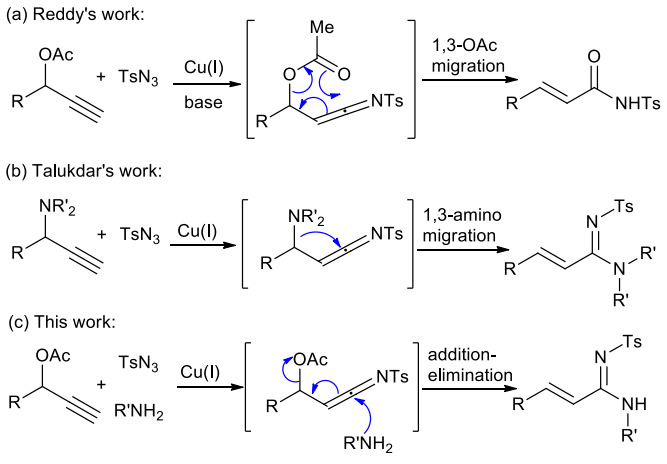
Acrylamidines were synthesized via the copper-catalyzed three-component reaction of propargyl acetates, sulfonyl azides and amines, which are readily accessible materials. The synthesized *N,N'*-bis(aryl)amidines could be converted into 2-styrylbenzoimidazoles by the iodobenzene-catalyzed oxidative C-H amination using mCPBA as terminal oxidant.

## Introduction

Since the breakthrough in the generation of ketenimines via the copper-catalyzed azide–alkyne cycloaddition (CuAAC)[1], the chemistry of ketenimines has emerged as a powerful tool in the synthesis of diverse nitrogen containing cyclic and acyclic motifs of biological and pharmaceutical interest[2]. Chang,[3] our group,[4] and others[5] have reported a number of elegant works that involve the transformation of ketenimines generated in situ by CuAAC route. Most recently, Reddy and coworkers developed a Cu-catalyzed conversion of propargyl acetates to α,β-unsaturated amides via the CuAAC process and the 1,3-migration of acetyl group ([3,3]-sigmatropic rearrangement) (Scheme 1a).[6] Similarly, Talukdar's group[7] converted propargyl amines to α,β- unsaturated amidines through 1,3-amino group migration of the *in situ* generated ketenimine intermediate (Scheme 1b). Encouraged by these results and in continuation of our interest in ketenimine chemistry, we herein report a three-component synthesis of acrylamindines via the Cu(I)-catalyzed reaction of readily accessible propargyl acetates, sulfonyl azides and amines, involving a formation of ketenimine and a nucleophilic addition-elimination process (Scheme 1c). The synthesized acrylamindines, i.e., α,β-unsaturated amidines, is an important class of nitrogen-containing compounds due to their synthetic applications.[8]




**Scheme 1** Previous works and our design.

## Results and discussion

Initially, we selected tosyl azide (**1a**), 1-phenylprop-2-ynyl acetate (**2a**) and aniline (**1c**) as the model substrates to test the feasibility of this transformation. When the reaction was performed in the presence of 10 mol % copper (I) bromide using $K_2CO_3$ as the base in acetonitrile at room temperature for 1 hour, α,β-unsaturated amidine **4a** was isolated in 60% yield (Table 1, entry 1). The addition of 4Å MS in the reaction system improved the yield to 76% (Table 1, entry 2). Shortening the reaction time led to a decrease in the yield of **4a** (Table 1, entry 3), while the formation of **4a** was not favoured when the reaction was performed for additional reaction time (Table 1, entry 4). Increasing the amount of aniline improved the yield to 85% (Table 1, entry 5). Changing the catalyst (Table 1, entries 6-8), base (Table 1, entries 9-11) or solvent (Table 1, entries 12-15) led to decreases in the yield of **4a**. The reaction proceeded at 0 °C for 3 hours and furnished **4a** with only 45% yield (Table 1, entry 16). Raising the reaction temperature to 50 °C also led to a decrease in the yield (Table 1, entry 17).

To establish the scope of methodology, the optimized conditions were applied to a wide range of substrates. As shown in Table 2, *p*-methylbenzenesulfonyl, phenylsulfonyl and p-methoxybenzenesulfonyl azides (**1a**-**1c**) gave the desired products **4a**-**4c** with satisfactory yields (Table 2, entries 1-3), whereas (naphthalen-2-ylsulfonyl, 4-(acetylamino)-

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† Footnotes relating to the title and/or authors should appear here.
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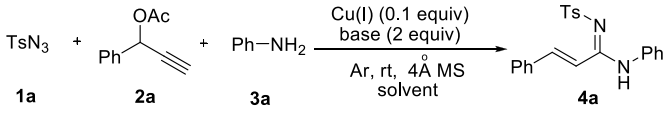
benzenesulfonyl, 4-nitrobenzenesulfonyl, 4-florobenzene-sulfonyl and methylsulfonyl azides (**1d-1h**) yielded in the corresponding products **4d**-4**h** in much lower yields (Table 2, entries 4-8). When the $R^2$ group on propargyl acetates **2** was 4-methoxyphenyl (**2b**), 4-methylphenyl (**2c**), styryl (**2d**), and 2-furanyl (**2e**), the corresponding products **4i**-4**l** were isolated in 54%-67% yields (Table 2, entries 9-12). In the case where $R^2$ was 4-nitrophenyl (**2f**), a lower yield (43%) of **4m** was obtained (Table 2, entry 13). The substituted anilines were also examined for their reaction with **1a** and **2a** under the standard conditions. 4-Methylaniline (**3b**), 4-methoxyaniline (**3c**), and 2-methylaniline (**3d**) gave the corresponding products **4n**-**4p** in good to excellent yields (Table 2, entries 14-16), whereas 4-chloroaniline (**3e**) furnished the desired product **4q** in poor yield due to the electron-withdrawing property of chlorine atom (Table 2, entry 17).

**Table 1.** Screening of the reaction conditions[a]



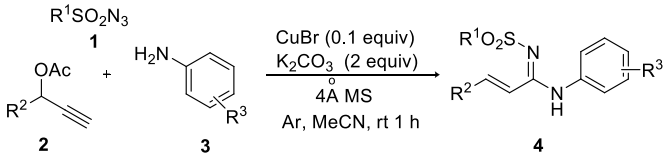

1a 2a 3a 4a

| entry | catalyst | base | **3a** (equiv) | solvent | time (h)[c] | Yield (%)[d] |
|---|---|---|---|---|---|---|
| 1 | CuBr | $K_2CO_3$ | 1 | MeCN | 1 | 60[b] |
| 2 | CuBr | $K_2CO_3$ | 1 | MeCN | 1 | 76 |
| 3 | CuBr | $K_2CO_3$ | 1 | MeCN | 0.5 | 57 |
| 4 | CuBr | $K_2CO_3$ | 1 | MeCN | 1.5 | 75 |
| 5 | CuBr | $K_2CO_3$ | 2 | MeCN | 1 | 85 |
| 6 | CuI | $K_2CO_3$ | 2 | MeCN | 1 | 71 |
| 7 | CuCl | $K_2CO_3$ | 2 | MeCN | 1 | 38 |
| 8 | CuOTf | $K_2CO_3$ | 2 | MeCN | 1 | 56 |
| 9 | CuBr | $Cs_2CO_3$ | 2 | MeCN | 1 | 40 |
| 10 | CuBr | pyridine | 2 | MeCN | 1 | 46 |
| 11 | CuBr | $NEt_3$ | 2 | MeCN | 1 | 42 |
| 12 | CuBr | $K_2CO_3$ | 2 | THF | 1 | 42 |
| 13 | CuBr | $K_2CO_3$ | 2 | DMF | 1 | 47 |
| 14 | CuBr | $K_2CO_3$ | 2 | PhMe | 1 | 23 |
| 15 | CuBr | $K_2CO_3$ | 2 | DCE | 1 | 46 |
| 16 | CuBr | $K_2CO_3$ | 2 | MeCN | 3 | 45[e] |
| 17 | CuBr | $K_2CO_3$ | 2 | MeCN | 1 | 49[f] |

[a] Reaction conditions: **1a** (0.5 mmol), **2a** (0.5 mmol), Cu salt (0.05 mmol), 4Å MS (100 mg), base (1.0 mmol), solvent (2 mL), room temperature; [b] Without 4 Å MS; [c] Reaction time was determined by TLC; [d] Isolated yield; [e] The reaction was carried out at 0 °C; [f] The reaction was carried out at 50 °C.

As a synthetic application of our methodology, we converted the synthesized *N,N'*-bis(aryl)amidines **4a**-4**h** (Table 3, entries 1-8) and **4n**-4**p** (Table 3, entries 9-11) into 2-styrylbenzoimidazoles **5a-5k** by the iodobenzene-catalyzed oxidative C-H amination in the presence of mCPBA as a terminal oxidant at room temperature (Table 3).[9] The reaction is general although the target products were obtained in lower yields in most cases. Taking into consideration of the great importance of benzoimidazoles in medicine chemistry[10] and organic materials, [11] our two-step approach provided a new strategy to construct 2-styrylbenzoimidazoles.

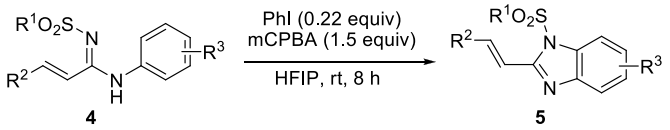
**Table 2.** Substrate scope of azides[a]




| entry | **1** ($R^1$) | **2** ($R^2$) | **3** ($R^3$) | **4**/yield (%)[b] |
|---|---|---|---|---|
| 1 | **1a** (4-$MeC_6H_4$) | **2a** | **3a** (H) | **4a**/ 88 |
| 2 | **1b** (Ph) | **2a** | **3a** | **4b**/ 67 |
| 3 | **1c** (4-$MeOC_6H_4$) | **2a** | **3a** | **4c**/ 97 |
| 4 | **1d** (2-naphthanenyl) | **2a** | **3a** | **4d**/ 34 |
| 5 | **1e** (4-$AcNHC_6H_4$) | **2a** | **3a** | **4e**/ 43 |
| 6 | **1f** (4-$NO_2C_6H_4$) | **2a** | **3a** | **4f**/ 26 |
| 7 | **1g** (4-$FC_6H_4$) | **2a** | **3a** | **4g**/ 39 |
| 8 | **1h** (Me) | **2a** | **3a** | **4h**/ 39 |
| 9 | **1a** | **2b** (4-$MeOC_6H_4$) | **3a** | **4i**/ 60 |
| 10 | **1a** | **2c** (4-$MeC_6H_4$) | **3a** | **4j**/ 67 |
| 11 | **1a** | **2d** (PhCH=CH) | **3a** | **4k**/ 63 |
| 12 | **1a** | **2e** (2-furanyl) | **3a** | **4l**/ 54 |
| 13 | **1a** | **2f** (4-$NO_2C_6H_4$) | **3a** | **4m**/ 43 |
| 14 | **1a** | **2a** | **3b** (4-Me) | **4n**/ 95 |
| 15 | **1a** | **2a** | **3c** (4-MeO) | **4o**/ 88 |
| 16 | **1a** | **2a** | **3d** (2-Me) | **4p**/ 84 |
| 17 | **1a** | **2a** | **3e** (4-Cl) | **4q**/ 20 |

[a] Reaction conditions: **1** (0.5 mmol), **2a** (0.5 mmol), **3a** (1 mmol), CuBr (0.05 mmol), 4Å MS (100 mg), acetonitrile (2 mL), Ar, room temperature, 1 h. [b] Product yields are given for compounds isolated after purification from a silica gel column.

**Table 3.** Preparation of benzoimidiazoles[a]




| entry | **4** ($R^1$/$R^2$/$R^3$) | **5**/ yield (%)[b] |
|---|---|---|
| 1 | **4a** (4-$MeC_6H_4$/Ph/H) | **5a**/ 64 |
| 2 | **4b** (Ph/Ph/H) | **5b**/ 44 |
| 3 | **4c** (4-$MeOC_6H_4$/Ph/H) | **5c**/ 45 |
| 4 | **4d** (2-naphthanenyl/Ph/H) | **5d**/ 44 |
| 5 | **4h** (Me/Ph/H) | **5e**/ 25 |
| 6 | **4f** (4-$NO_2C_6H_4$/Ph/H) | **5f**/ 22 |
| 7 | **4g** (4-$FC_6H_4$/Ph/H) | **5g**/ 41 |
| 8 | **4e** (4-$AcNHC_6H_4$/Ph/H) | **5h**/ 29 |
| 9 | **4o** (4-$MeC_6H_4$/Ph/4-MeO) | **5i**/ 30 |
| 10 | **4n** (4-$MeC_6H_4$/Ph/4-Me) | **5j**/ 36 |
| 11 | **4p** (4-$MeC_6H_4$/Ph/2-Me) | **5k**/ 30 |

[a] Reaction conditions: **4** (0.2 mmol), PhI (5 μL), mCPBA (0.3 mmol), HFIP (0.4 mL), room temperature, 8 h. [b] Product yields are given for compounds isolated after purification from a silica gel column.

## Conclusions

We developed a copper-catalyzed three-component synthesis of α,β-unsaturated amidines from propargyl acetates, sulfonyl azides and amines, which are readily accessible materials. The reaction proceeded through a cascade process involving ketenimine formation via copper-catalyzed alkyne-azide cycloaddition, nucleophilic addition of amine to ketenimine, and elimination of acetate. Furthermore, the synthesized *N,N'*-bis(aryl)amidines could be converted into 2-styrylbenzoimidazoles by the iodobenzene-catalyzed oxidative C-H amination using mCPBA as terminal oxidant.

## Experimental section

### General methods

Infrared spectra were obtained on a FTIR spectrometer. $^1$H NMR spectra were recorded on 400 MHz spectrometer, referred to the internal solvent signals (0 for TMS in $CDCl_3$ or 2.5 for the residue of DMSO). The following abbreviations were used to describe peak patterns where appropriate: b = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Coupling constants were reported in Hertz (Hz). $^{13}$C NMR were recorded on 100 MHz spectrometer, referred to the internal solvent signals (77.27 for $CDCl_3$ or 40.0 for DMSO-$d_6$). High resolution mass spectra (HRMS) were performed on an electron ionization time-of-flight (EI-TOF) mass spectrometer. Matrix-Assisted Laser Desorption/ Ionization Time of Flight Mass Spectrometry (MALDITOF-MS) were experienced with Bruker's ultrafleXtreme. Melting points were uncorrected and measured with a micro melting point apparatus.

### General procedure for the synthesis of (*E*)-acrylimidamide 4

To a solution of $K_2CO_3$ (1.0 mmol), 4Å MS (100 mg) and CuBr (0.05 mmol) in MeCN (0.5 mL) protected by Argon was added sulfonyl azide **1** (0.5 mmol) in MeCN (0.5 mL), 2-yn-1-yl acetate **2** (0.5 mmol) in MeCN (0.5 mL) and aniline **3** (0.5 mmol) in MeCN (0.5 mL) in turns via syringe, and the mixture was reacted at room temperature for 1 h. After filtrated, the reaction mixture was then diluted with $CH_2Cl_2$ (10 mL), washed with water and brine, dried over anhydrous $Na_2SO_4$, and evaporated in vacuum. The residue was subject to silica gel column chromatography with EA/Pet (1:3, v/v) as eluent to give pure product 4.

**(*E*)-*N*-Phenyl-*N*'-tosylcinnamimidamide (4a)**

A yellow powder (166 mg, 88%); m.p. 170.0-171.6 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 10.14 (b, 1H), 7.93 (d, J = 8.4 Hz, 2H), 7.85 (d, *J* = 15.6 Hz, 1H), 7.42 (dd, J1 = 7.6 Hz, J2 = 7.2 Hz, 2H), 7.37 - 7.27 (m, 8H), 7.19 (d, *J* = 7.6, 2H), 6.51 (d, *J* = 11.2 Hz, 1H), 2.43 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 160.2, 144.7, 143.1, 140.0, 136.6, 134.7, 130.7, 129.8, 129.7, 129.1, 128.5, 127.8, 126.7, 117.8, 21.8; IR (neat) *v* 3298, 3060, 3021, 1635, 1561, 1519, 1445, 1389, 1350, 1276, 1142, 1089, 758, 691 cm$^{-1}$; HRMS (EI) calcd for Chemical Formula: $C_{22}H_{20}N_2O_2S$, 376.1245; found, 376.1241.

**(*E*)-*N*-Phenyl-*N*'-(phenylsulfonyl)cinnamimidamide (4b)**

A yellow powder (121 mg, 67%); m.p. 164.1-165.3 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 10.16 (b, 1H), 8.05 (d, J = 8.4 Hz, 2H), 7.87 (d, *J* = 15.2 Hz, 1H), 7.59 - 7.50 (m, 3H), 7.43 (dd, $J_1$ = 8.0 Hz, $J_2$ = 7.2 Hz, 2H), 7.37 - 7.29 (m, 6H), 7.19 (d, *J* = 7.2 Hz, 2H), 6.51 (b, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 160.4, 142.8, 136.5, 134.6, 132.5, 130.8, 129.9, 129.1, 129.1, 128.6, 127.9, 126.6, 126.1, 117.7; IR (neat) v 3299, 33048, 3026, 1635, 1561, 1518, 1445, 1397, 1346, 1277, 1143, 1089, 754, 689 cm-1; HRMS (EI) calcd for $C_{21}H_{18}N_2O_2S$, 362.1089; found, 362.1084.

**(*E*)-*N*'-((4-methoxyphenyl)sulfonyl)-*N*-phenyl cinnamimidamide (4c)**

A yellow powder (191 mg, 97%); m.p. 146.2-47.5 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 10.11 (b, 1H), 7.98 (d, *J* = 8.8 Hz, 2H), 7.83 (d, *J* = 15.2 Hz, 1H), 7.42 (dd, $J_1$ = 7.6 Hz, $J_2$ = 7.2 Hz, 2H), 7.36 - 7.28 (m, 6H), 7.19 (d, *J* = 6.8 Hz, 2H), 6.98 (d, J = 9.2 Hz, 2H), 6.52 (b, 1H), 3.86 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 162.8, 160.0, 144.5, 136.7, 134.8, 134.7, 130.7, 129.8, 129.1, 128.7, 128.5, 127.8, 126.0, 117.8, 114.2, 55.8; IR (neat) v 3293, 3060, 2944, 2837, 1650, 1596, 1562, 1519, 1497, 1444, 1257, 1141, 1090, 1026, 805, 759, 692 cm$^{-1}$; HRMS (EI) calcd for $C_{22}H_{20}N_2O3S$, 392.1195; found, 392.1190.

**(*E*)-*N*'-(Naphthalen-1-ylsulfonyl)-*N*-phenylcinnamimidamide (4d)**

A light yellow powder (71 mg, 34%); m.p. 167.0-168.2 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 10.23 (b, 1H), 8.59 (s, 1H), 8.05 (dd, $J_1$ = 8.4 Hz, $J_2$ = 1.6 Hz, 1H), 7.98 (d, *J* = 8.4 Hz, 2H), 7.92 - 7.85 (m, 2H), 7.64 - 7.57 (m, 2H), 7.43 (dd, $J_1$ = $J_2$ = 7.6 Hz, 2H), 7.36 - 7.28 (m, 6H), 7.21 (d, J = 7.2 Hz, 2H), 6.53 (b, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 160.4, 139.7, 136.5, 135.0, 134.6, 132.4, 130.8, 129.9, 129.6, 129.4, 129.1, 128.7, 128.6, 128.1, 127.9, 127.5, 127.3, 126.1, 122.7, 117.7; IR (neat) v 3289, 3054, 1635, 1563, 1520, 1445, 1382, 1348, 1278, 1143, 1124, 1073, 756, 690 cm$^{-1}$; HRMS (EI) calcd for $C_{25}H_{20}N_2O_2S$, 412.1245; found, 412.1252.

***N*-(4-((*E*)-*N*-((*E*)-3-Phenyl-1-(phenylamino)allylidene) sulfamoyl)phenyl)acetamide (4e)**

A yellow powder (90 mg, 43%); m.p. 172.2-173.5 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 10.10 (b, 1H), 8.01 (s, 1H), 7.93 (d, J = 8.8 Hz, 2H), 7.82 (d, J = 14.8 Hz, 1H), 7.67 (d, J = 7.6 Hz, 2H), 7.42 (dd, $J_1$ = 7.2 Hz, *J*2 = 8.0 Hz, 2H), 7.36 - 7.28 (m, 6H), 7. 17 (d, J = 5.2 Hz, 2H), 6.50 (b, 1H), 2.20 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 169.2, 160.4, 145.0, 142.0, 137.4, 136.4, 134.5, 130.8, 129.9, 129.1, 128.6, 128.0, 127.7, 126.1, 119.6, 117.6, 24.9; IR (neat) v 3315, 3048, 2920, 1676, 1635, 1593, 1519, 1446, 1400, 1315, 1262, 1141, 1091, 754 cm$^{-1}$; HRMS (EI) calcd for $C_{23}H_{21}N3O_3S$, 419.1304; found, 419.1305.

**(*E*)-*N'*-((4-Nitrophenyl)sulfonyl)-*N*-phenylcinnamimidamide (4f)**

A white powder (53 mg, 26%); m.p. 148.8-149.6 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 10.15 (b, 1H), 8.37 (d, *J* = 8.8 Hz, 2H), 8.23 (d, *J* = 8.8 Hz, 2H), 7.87 (d, *J* = 13.6 Hz, 1H), 7.47 (dd, $J_1 = J_2$ = 7.6 Hz, 2H), 7.42 - 7.32 (m, 6H), 7.22 (d, *J* = 7.2 Hz, 2H), 6.52 (b, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 161.1, 150.0, 148.5, 146.1, 136.1, 134.3, 131.2, 130.0, 129.2, 128.7, 128.4, 127.9, 126.2, 124.4, 117.0; IR (neat) ν 3319, 3024, 1635, 1521, 1447, 1348, 1262, 1145, 1092, 745, 680 cm$^{-1}$; MALDITOF-MS (DHB) calcd for $C_{21}H_{18}N_3O_4S$ $[M+H]^+$, 408.102; found, 408.101.

**(*E*)-*N*'-((4-Fluorophenyl)sulfonyl)-*N*-phenylcinnamimidamide (4g)**

A yellow powder (74 mg, 39%); m.p. 162.6-163.5 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 10.12 (b, 1H), 8.07 - 8.04 (m, 2H), 7.85 (d, *J* = 14.4 Hz, 1H), 7.44 (dd, $J_1$ = 7.2 Hz, $J_2$ = 8.0 Hz, 2H), 7.36 - 7.30 (m, 6H), 7.21 - 7.17 (m, 4H), 6.53 (b, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 165.1 (d, $J_{C\text{-}F}$ = 252 Hz), 160.4, 145.1, 139.0 (d, $J_{C\text{--}F}$ = 3.1 Hz), 136.4, 134.6, 130.9, 129.9, 129.3(d, $J_{C\text{-}F}$ = 9.2 Hz), 129.2, 128.6, 128.0, 126.1, 117.6, 116.2(d, $J_{C\text{-}F}$ = 22.4 Hz); IR (neat) *ν* 3424, 2997, 2911, 1636, 1518, 1494, 1445, 1281, 1146, 1092, 1028, 953, 762, 696 cm$^{-1}$; HRMS (EI) calcd for $C_{21}H_{17}FN_2O_2S$, 380.0995; found, 380.0994.

**(*E*)-*N*'-(Methylsulfonyl)-*N*-phenylcinnamimidamide (4h)**

A yellow oil (59 mg, 39%); $^1$H NMR (400 MHz, $CDCl_3$) δ 9.86 (b, 1H), 7.85 (d, *J* = 11.2 Hz, 1H), 7.45 - 7.39 (m, 4H), 7.38 - 7.31 (m, 4H), 7.22 (d, *J* = 5.2 Hz, 2H), 6.55 (b, 1H), 3.16 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 160.2, 144.3, 136.5, 134.6, 130.7, 129.8, 129.2, 128.5, 127.8, 125.9, 117.8, 42.9; IR (neat) ν 3290, 3057, 3024, 2929, 1637, 1577, 1525, 1445, 1275, 1124, 1028, 969, 791, 758, 692 cm$^{-1}$; HRMS (EI) calcd for $C_{16}H_{16}N_2O_2S$, 300.0932; found, 300.0933

**(*1E,2E*)-3-(4-Methoxyphenyl)-*N*-phenyl-*N*'-tosylacryl imidamide (4i)**

A yellow powder (123 mg, 60%); m.p. 174.8176.2 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 10.08 (b, 1H), 7.92 (d, *J* = 8.4 Hz, 2H), 7.82 (d, *J* = 15.2 Hz, 1H), 7.42 (dd, $J_1 = J_2$ = 7.6 Hz, 2H), 7.36 - 7.30 (m, 5H), 7.18 (d, *J* = 7.6 Hz, 2H), 6.83 (d, *J* = 8.8 Hz, 2H), 6.38 (d, *J* = 14.0 Hz, 1H), 3.80 (s, 3H), 2.42 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 161.8, 160.6, 143.0, 140.1, 136.8, 130.4, 129.8, 129.6, 127.7, 127.5, 126.6, 126.1, 115.1, 114.6, 55.6, 21.8; IR (neat) ν 3304, 3060, 2965, 2929, 2834, 1633, 1601, 1558, 1510, 1444, 1254, 1174, 1141, 1090, 1029, 825, 757, 691 cm$^{-1}$; HRMS (EI) calcd for $C_{23}H_{22}N_2O_3S$, 406.1351; found, 406.1350.

**(*1E,2E*)-*N*-Phenyl-3-(p-tolyl)-N'-tosylacrylimidamide (4j)**

A yellow powder (131 mg, 67%); m.p. 166.7-168.0 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 10.11 (b, 1H), 7.92 (d, *J* = 8.4 Hz, 2H), 7.83 (d, *J* = 15.2 Hz, 1H), 7.42 (dd, $J_1 = J_2$ = 7.6 Hz, 2H), 7.35 (d, *J* = 7.2 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 6.4 Hz, 2H), 7.18 (d, *J* = 7.6 Hz, 2H), 7.12 (d, *J* = 6.4 Hz, 2H), 6.47 (b, 1H), 2.42 (s, 3H), 2.33 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 160.5, 144.9, 143.1, 141.3, 140.0, 136.7, 132.0, 129.9, 129.8, 129.7, 128.6, 127.8, 126.7, 126.1, 116.6, 21.8, 21.7; IR (neat) ν 3300 3054, 2920, 1634, 1599, 1561, 1520, 1444, 1275, 1142, 1089, 810, 757 cm$^{-1}$; HRMS (EI) calcd for $C_{23}H_{22}N_2O_2S$, 390.1402; found, 390.1402.

**(*1E,2E,4E*)-*N*,5-Diphenyl-N'-tosylpenta-2,4-dienimidamide (4k)**

A yellow powder (127 mg, 63%); m.p. 170.6-172.2 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 10.03 (b, 1H), 7.91 (d, J = 8.0 Hz, 2H), 7.63 (dd, $J_1$ = 12.4 Hz, $J_2$ = 13.2 Hz, 1H), 7.43 - 7.38 (m, 4H), 7.35 - 7.28 (m, 6H), 7.16 (d, *J* = 7.6, 2H), 6.89 (d, *J* = 15.6 Hz, 1H), 6.73 (dd, $J_1$ = 15.6 Hz, $J_2$ = 11.2 Hz, 1H), 6.07 (b, 1H), 2.42 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 160.3, 145.1, 143.0, 141.6, 140.1, 136.7, 136.1, 130.0, 129.6, 129.5, 129.0, 127.8, 127.5, 126.6, 126.2, 120.8, 21.8; IR (neat) ν 3297, 3059, 3021, 1622, 1557, 1444, 1386, 1352, 1276, 1142, 1090, 996, 748, 691 cm$^{-1}$; HRMS (EI) calcd for $C_{24}H_{22}N_2O_2S$, 402.1402; found, 402.1406.

**(*1E,2E*)-3-(Furan-2-yl)-*N*-phenyl-*N'*-tosylacrylimidamide (4l)**

A yellow powder (98 mg, 54%); m.p. 120.5-121.4 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 10.09 (b, 1H), 7.91 (d, *J* = 8.0 Hz, 2H), 7.64 (d, *J* = 16.8 Hz, 1H), 7.45 - 7.29 (m, 6H), 7.17 (d, *J* = 7.6 Hz, 2H), 6.58 (d, *J* = 3.6 Hz, 1H), 6.43 - 6.37 (m, 2H), 2.42 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 160.2, 151.3, 145.4, 143.1, 140.1, 136.6, 131.1, 129.8, 129.6, 127.9, 126.6, 126.2, 116.3, 115.1, 112.8, 21.8; IR (neat) *ν* 3286, 2956, 2923, 2851, 1733, 1635, 1571, 1515, 1444, 1378, 1276, 1142, 1090, 1017, 744 cm$^{-1}$; HRMS (EI) calcd for $C_{20}H_{18}N_2O_3S$, 366.1038; found, 366.1039.

**(*1E,2E*)-3-(4-Nitrophenyl)-*N*-phenyl-*N*'-tosylacrylimidamide (4m)**

A yellow powder (91 mg, 43%); m.p. 222.4-223.2 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 10.22 (b, 1H), 8.17 (d, *J* = 8.8 Hz, 2H), 7.93 (d, *J* = 8.4 Hz, 2H), 7.84 (d, *J* = 14.4 Hz, 1H), 7.50 - 7.44 (m, 4H), 7.39 (dd, $J_1$ = 7.6 Hz, $J_2$ = 6.8 Hz, 1H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 6.8, 2H), 6.61 (d, *J* = 14.4 Hz, 1H), 2.44 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 159.0, 148.6, 143.5, 141.4, 140.7, 139.5, 136.3, 130.0, 129.8, 129.0, 128.3, 126.7, 126.1, 124.4, 122.1, 21.8; IR (neat) ν 3289, 1599, 1560, 1519, 1445, 1343, 1276, 1143, 1089, 758, 692 cm$^{-1}$; HRMS (EI) calcd for $C_{22}H_{19}N_3O_4S$, 421.1096; found, 421.1088.

**(*E*)-*N*-(*p*-Tolyl)-*N*'-tosylcinnamimidamide (4n)**

A yellow powder (185 mg, 95%); m.p. 169.4-170.7 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 10.08 (b, 1H), 7.92 (d, *J* = 8.4 Hz, 2H), 7.85 (d, *J* = 15.2 Hz, 1H), 7.37 - 7.30 (m, 7H), 7.21 (d, *J* = 8.4 Hz, 2H), 7.05 (d, *J* = 8.4 Hz, 2H), 6.49 (d, *J* = 14.0 Hz, 1H), 2.42 (s, 3H), 2.39 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 160.3, 144.7, 143.1, 140.0, 134.7, 133.9, 130.6, 130.4, 129.6, 129.1, 128.5, 127.3, 126.6, 126.0, 117.8, 21.8, 21.3; IR (neat) ν 3298, 3021, 2920, 2858, 1745, 1640, 1557, 1510, 1449, 1407, 1275, 1139, 1088, 815, 760, 694 cm$^{-1}$; HRMS (EI) calcd for $C_{23}H_{22}N_2O_2S$, 390.1402; found, 390.1405.

**(*E*)-*N*-(4-Methoxyphenyl)-*N*'-tosylcinnamimidamide (4o)**

A light yellow powder (178 mg, 88%); m.p. 150.3-151.5 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 10.01 (b, 1H), 7.93 (d, *J* = 8.0 Hz, 2H),

7.85 (d, *J* = 15.2 Hz, 1H), 7.36 - 7.30 (m, 7H), 7.09 (d, *J* = 8.0 Hz, 2H), 6.93 (d, *J* = 8.8 Hz, 2H), 6.43 (d, *J* = 15.2 Hz, 1H), 3.85 (s, 3H), 2.43 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 160.6, 159.3, 144.7, 143.1, 140.1, 134.7, 130.6, 129.6, 129.2, 129.1, 128.5, 127.9, 126.6, 117.6, 115.0, 55.8, 21.8; IR (neat) ν 3298, 3021, 2926, 2828, 1636, 1557, 1509, 1449, 1250, 1138, 1088, 1031, 808, 760, 694 cm$^{-1}$; HRMS (EI) calcd for $C_{23}H_{22}N_2O_3S$, 406.1351; found, 406.1353.

**(*E*)-*N*-(*o*-Tolyl)-*N*'-tosylcinnamimidamide (4p)**

A light yellow powder (163 mg, 84%); m.p. 113.6-114.8 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 9.96 (b, 1H), 7.94 (d, *J* = 8.0 Hz, 2H), 7.90 (d, *J* = 15.2 Hz, 1H), 7.35 – 7.29 (m, 9H), 7.27 - 7.23 (m, 1H), 7.12 (d, *J* = 7.2 Hz, 1H), 6.33 (d, *J* = 15.2 Hz, 1H), 2.43 (s, 3H), 2.24 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 160.6, 145.0, 143.1, 140.0, 135.2, 134.8, 134.7, 131.6, 130.8, 129.7, 129.1, 128.6, 128.6, 127.6, 127.3, 126.7, 117.3, 21.8, 18.2; IR (neat) ν 3271, 3060, 3021, 1637, 1557, 1449, 1386, 1275, 1138, 1084, 758, 694 cm$^{-1}$; HRMS (EI) calcd for $C_{23}H_{22}N_2O_2S$, 390.1402; found, 390.1408.

**(*E*)-*N*-(*m*-Tolyl)-*N*'-tosylcinnamimidamide (4q)**

A light yellow powder (98 mg, 84%); m.p. 186.7-187.7 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 10.11 (b, 1H), 7.92 (d, *J* = 8.4 Hz, 2H), 7.85 (d, *J* = 14.8 Hz, 1H), 7.37 - 7.28 (m, 8H), 7.16 (d, *J* = 7.6 Hz, 1H), 7.00 - 6.96 (m, 2H), 6.52 (d, *J* = 13.6 Hz, 1H), 2.43 (s, 3H), 2.38 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 160.2, 144.6, 143.1, 140.1, 140.0, 136.5, 134.7, 130.7, 129.7, 129.6, 129.1, 128.7, 128.6, 126.7, 123.2, 117.9, 21.8, 21.6; IR (neat) ν 3291, 2920, 1637, 1563, 1525, 1486, 1447, 1276, 1143, 1087, 811, 781, 760 cm$^{-1}$; HRMS (EI) calcd for $C_{23}H_{22}N_2O_2S$, 390.1402; found, 390.1399.

**(*E*)-*N*-(4-Chlorophenyl)-*N*'-tosylcinnamimidamide (4r)**

A white powder (42 mg, 20%); m.p. 193.1-193.8 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 10.06 (b, 1H), 7.91 (d, *J* = 8.0 Hz, 2H), 7.83 (d, *J* = 14.4 Hz, 1H), 7.40 - 7.30 (m, 9H), 7.14 (d, *J* = 7.6, 2H), 6.48 (b, 1H), 2.43 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 160.0, 143.3, 139.8, 135.2, 134.5, 130.9, 130.0, 129.7, 129.2, 128.6, 127.2, 126.7, 117.4, 100.2, 21.8; IR (neat) *v* 3295, 2975, 1635, 1513, 1491, 1401, 1273, 1143, 1088, 688 cm$^{-1}$; HRMS (EI) calcd for $C_{22}H_{19}ClN_2O_2S$, 410.0856; found, 410.0851.

## General procedure for the synthesis of (*E*)-2-vinyl-1-sulfonyl-1*H*-benzo[*d*]imidazole (5)

The mixture of (*E*)-acrylimidamide **4** (0.2 mmol), PhI (5.0 μL) and m-CPBA (0.3 mmol) in HFIP (0.4 mL) was stirred at room temperature for 8 h, and then subjected to silica gel column chromatography with EA/Pet (1:4, v/v) as eluent to give pure product **5**.

**(*E*)-2-Styryl-1-tosyl-1H-benzo[*d*]imidazole (5a)**

A fresh solid (48 mg, 64%); m.p. 152.1-153.5 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.11 - 8.06 (m, 1H), 7.92 (s, 2H), 7.78 (d, *J* = 8.4 Hz, 2H), 7.70 - 7.66 (m, 3H), 7.46 - 7.33 (m, 5H), 7.22 (d, *J* = 8.4 Hz, 2H), 2.34 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 151.4, 146.2, 142.9, 140.1, 136.0, 135.5, 133.4, 130.4, 129.9, 129.2, 128.0, 127.1, 125.5, 125.3, 120.1, 114.6, 114.2, 21.9; IR (neat) ν 3099, 3050, 3018, 2923, 2852, 1625, 1396, 1512, 1448, 1378, 1344, 1200, 1167, 1121, 1089, 1050, 811, 764, 670 cm$^{-1}$; HRMS (EI) calcd for $C_{22}H_{18}N_2O_2S$, 374.1089; found, 374.1086.

**(*E*)-1-(Phenylsulfonyl)-2-styryl-1*H*-benzo[d]imidazole (5b)**

A yellow oil (32 mg, 44%); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.11 - 8.07 (m, 1H), 7.93 - 7.89 (m, 4H), 7.72 - 7.66 (m, 3H), 7.57 (dd, $J_1$ = $J_2$ = 7.6 Hz, 1H), 7.47 - 7.43 (m, 4H), 7.41 - 7.34 (m, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 151.4, 142.9, 140.2, 138.5, 136.0, 134.8, 133.4, 129.9, 129.8, 129.2, 128.0, 127.0, 125.6, 125.4, 120.2, 114.5, 114.2; IR (neat) ν 3057, 3021, 1625, 1513, 1379, 1344, 1201, 1167, 1088, 1049, 749, 723, 684, 649 cm$^{-1}$; HRMS (EI) calcd for $C_{21}H_{16}N_2O_2S$, 360.0932; found, 360.0931.

**(E)-1-((4-Methoxyphenyl)sulfonyl)-2-styryl-1*H*-benzo[*d*]imidazole (5c)**

A pink oil (36 mg, 45%); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.09 - 8.07 (m, 1H), 7.93 (d, *J* = 2.4 Hz, 2H), 7.84 (d, *J* = 9.2 Hz, 2H), 7.70 - 7.66 (m, 3H), 7.46 - 7.33 (m, 5H), 6.87 (d, *J* = 8.8 Hz, 2H), 3.78 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 164.6, 151.4, 142.9, 140.0, 136.0, 133.4, 129.9, 129.8, 129.4, 129.2, 128.0, 125.5, 125.3, 120.1, 115.0, 114.7, 114.2, 56.0; IR (neat) ν 3060, 3025, 1593, 1497, 1448, 1377, 1343, 1266, 1201, 1164, 1090, 1050, 745, 674 cm$^{-1}$; HRMS (EI) calcd for $C_{22}H_{18}N_2O_3S$, 390.1038; found, 390.1035.

**(E)-1-(naphthalen-2-ylsulfonyl)-2-styryl-1H-benzo[d]imidazole (5d)**

A yellow oil (36 mg, 44%); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, *J* = 1.6 Hz, 1H), 8.16 - 8.13 (m, 1H), 8.04 - 7.89 (m, 3H), 7.84 (dd, $J_1$ = 7.2, $J_2$ = 10.4 Hz, 2H), 7.46 (dd, $J_1$ = 8.8, $J_2$ = 2.0 Hz, 1H), 7.69 - 7.56 (m, 5H), 7.48 - 7.34 (m, 5H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 151.4, 142.9, 140.3, 136.0, 135.7, 135.2, 133.4, 132.0, 130.4, 130.1, 129.9, 129.8, 129.2, 129.1, 128.3, 128.2, 128.0, 125.6, 125.4, 121.3, 120.2, 114.7, 114.2; IR (neat) ν 3057, 3027, 2920, 2852, 1625, 1512, 1448, 1380, 1345, 1231, 1199, 1167, 1072, 1050, 857, 811, 746, 662 cm$^{-1}$; HRMS (EI) calcd for $C_{25}H_{18}N_2O_2S$, 410.1089; found, 410.1086.

**(E)-1-(methylsulfonyl)-2-styryl-1H-benzo[d]imidazole (5e)**

A yellow solid (15 mg, 25%); m.p. 192.4 - 193.4 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 16.0 Hz, 1H), 7.95 - 7.93 (m, 1H), 7.80 - 7.74 (m, 2H), 7.66 - 7.64 (m, 2H), 7.45 - 7.36 (m, 5H), 3.24 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 151.2, 142.9, 140.8, 135.8, 133.3, 130.0, 129.2, 128.1, 125.8, 125.5, 120.4, 113.9, 113.7, 42.6; IR (neat) ν 2923, 2846, 1626, 1513, 1172, 1233, 1200, 1163, 1144, 1054, 964, 764, 739, 696 cm$^{-1}$; HRMS (EI) calcd for $C_{16}H_{14}N_2O_2S$, 298.0776; found, 298.0780.

**(*E*)-1-((4-Nitrophenyl)sulfonyl)-2-styryl-1*H*-benzo[*d*]imidazole (5f)**

A yellow oil (18 mg, 22%); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 9.2 Hz, 2H), 8.16 - 8.03 (m, 3H), 7.97 - 7.85 (m, 2H), 7.72 - 7.66 (m, 3H), 7.49 - 7.37 (m, 5H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 151.3, 151.3, 143.5, 143.1, 141.2, 135.6, 132.9, 130.3, 129.3, 128.4, 128.1, 126.3, 125.9, 125.1, 120.6, 114.0, 113.8; IR (neat) ν 3099, 2923, 2846, 1730, 1625, 1533, 1387, 1346, 1231, 1200, 1167, 1087, 1048, 854, 759, 680 cm$^{-1}$; HRMS (EI) calcd for $C_{21}H_{15}N_3O_4S$, 405.0783; found, 405.0780.

**(*E*)-1-((4-Fluorophenyl)sulfonyl)-2-styryl-1*H*-benzo[*d*]imidazole (5g)**

A yellow oil (31 mg, 41%); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.09 - 8.04 (m, 1H), 7.96 - 7.88 (m, 4H), 7.71 - 7.66 (m, 3H), 7.47 - 7.35 (m, 5H), 7.14 - 7.08 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 166.3 (d, $J_{C\text{-}F}$ = 257.2 Hz), 151.3, 143.0, 140.5, 135.9, 134.4 (d, $J_{C\text{-}F}$ = 3.4 Hz), 133.2, 130.0, 129.9, 129.3, 128.0, 125.8, 125.5, 120.3, 117.4, 117.2, 114.2 (d, $J_{C\text{-}F}$ = 21.6 Hz); IR (neat) v 3102, 3066, 3027, 2923, 2855, 1626, 1590, 1514, 1493, 1449, 1382, 1344, 1242, 1200, 1087, 1049, 836, 750, 675 cm$^{-1}$; HRMS (EI) calcd for $C_{21}H_{15}FN_2O_2S$, 378.0838; found, 378.0836.

**(*E*)-*N*-(4-((2-Styryl-1H-benzo[*d*]imidazol-1-yl)sulfonyl)phenyl) acetamide (5h)**

A yellow solid (24 mg, 29%); m.p. 106.1-107.2 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.08 - 8.06 (m, 1H), 7.91 (s, 2H), 7.84 (d, *J* = 8.8 Hz, 2H), 7.70 - 7.63 (m, 3H), 7.59 (d, *J* = 8.8 Hz, 2H), 7.46 - 7.34 (m, 6H), 2.15 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 168.7, 151.4, 143.7, 142.9, 140.2, 136.0, 133.3, 132.8, 129.9, 129.2, 128.6, 128.0, 125.6, 125.4, 120.2, 119.6, 114.6, 114.2, 25.0; IR (neat) v 3316, 3101, 2293, 1697, 1589, 1531, 1376, 1313, 1263, 1230, 1166, 1084, 1046 cm$^{-1}$; HRMS (EI) calcd for $C_{23}H_{19}N_3O_3S$, 417.1147; found, 417.1142.

**(*E*)-6-Methoxy-2-styryl-1-tosyl-1*H*-benzo[d]imidazole (5i)**

A yellow solid (24 mg, 30%); m.p. 132.6 - 133.6 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.90 - 7.80 (m, 2H), 7.77 (d, *J* = 8.4 Hz, 2H), 7.65 - 7.61 (m, 3H), 7.56 (d, *J* = 8.8 Hz, 1H), 7.45 - 7.36 (m, 3H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.97 (dd, $J_1$ = 2.4, $J_2$ = 8.8 Hz, 1H), 3.92 (s, 3H), 2.35 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 158.3, 150.4, 146.2, 138.8,137.2, 136.2, 135.6, 134.3, 130.4, 129.6, 129.2, 127.9, 127.0, 120.5, 114.8, 114.2, 98.5, 56.3, 21.9; IR (neat) v 3024, 2917, 2846, 1736, 1625, 1596, 1510, 1447, 1378, 1021, 1170, 1089, 1045, 812, 753, 668 cm$^{-1}$; HRMS (EI) calcd for $C_{23}H_{20}N_2O_3S$, 404.1195; found, 404.1198.

**(*E*)-6-Methyl-2-styryl-1-tosyl-1*H*-benzo[d]imidazole (5j)**

A yellow solid (28 mg, 36%); m.p. 183.2-184.7 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 3.0 Hz, 3H), 7.77 (d, *J* = 8.4 Hz, 2H), 7.66 - 7.64 (m, 2H), 7.56 (d, *J* = 8.4 Hz, 1H), 7.46 - 7.42 (m, 2H), 7.40 - 7.38 (m, 1H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.57 (dd, $J_1$ = 1.2, $J_2$ = 8.4 Hz, 1H), 2.52 (s, 3H), 2.34 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 150.8, 146.1, 141.0, 139.5, 136.1, 135.7, 133.6, 130.4, 129.7, 129.2, 128.4, 127.9, 127.0, 127.0, 119.6, 114.8, 114.2, 22.4, 21.9; IR (neat) v 3390, 3063, 2920, 2846, 1739, 1623, 1593, 1447, 1378, 1200, 1170, 1147, 1089, 1043, 812, 748 cm$^{-1}$; HRMS (EI) calcd for $C_{23}H_{20}N_2O_2S$, 388.1245; found, 388.1245.

**(*E*)-4-Methyl-2-styryl-1-tosyl-1H-benzo[d]imidazole (5k)**

A flesh solid (23 mg, 30%); m.p. 165.3-166.3 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.93 (s, 2H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.77 (d, *J* = 8.4 Hz, 2H), 7.69 - 7.66 (m, 2H), 7.46 - 7.37 (m, 3H), 7.24 - 7.20 (m, 3H), 7.15 (d, *J* = 7.6 Hz, 1H), 2.63 (s, 3H), 2.33 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 150.6, 146.0, 142.2, 139.7, 136.2, 135.6, 133.1, 130.4, 129.7, 129.2, 128.4, 128.0, 127.1, 126.0, 125.2, 115.0, 111.6, 21.9, 16.8; IR (neat) v 3060, 3027, 2923, 2852, 1636, 1597, 1512, 1447, 1376, 1344, 1200, 1176, 1101, 1016, 972, 814, 759 cm$^{-1}$; HRMS (EI) calcd for $C_{23}H_{20}N_2O_2S$, 388.1245; found, 388.1249.

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