EurJOC
European Journal of Organic Chemistry

Chemistry Europe
European Chemical Societies Publishing

Accepted Article

Title: H-*BEA Zeolite-catalyzed Nucleophilic Substitution in Allyl Alcohols Using Sulfonamides, Amides, and Anilines

Authors: Akimichi Ohtsuki, Shunsuke Aoki, Ryo Nishida, Sachiko Morita, Takeshi Fujii, and Kazu Okumura

To be cited as: *Eur. J. Org. Chem.* 10.1002/ejoc.202000296

Link to VoR: https://doi.org/10.1002/ejoc.202000296

WILEY-VCH

10.1002/ejoc.202000296

WILEY-VCH

H-*BEA Zeolite-catalyzed Nucleophilic Substitution in Allyl Alcohols Using Sulfonamides, Amides, and Anilines

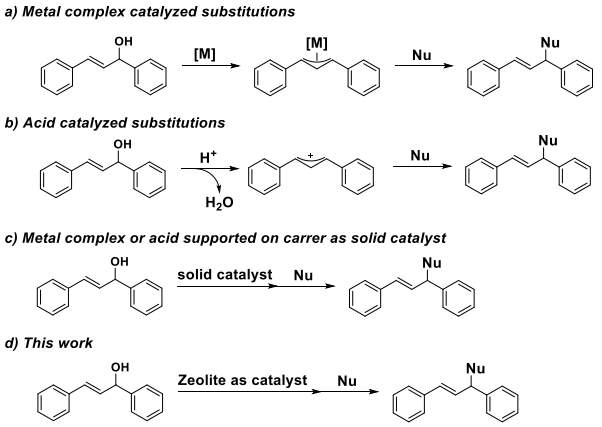
Akimichi Ohtsuki, *[a] Shunsuke Aoki, [a] Ryo Nishida, [a] Sachiko Morita, [a] Takeshi Fujii, [a] Kazu Okumura *[a]

Abstract: Herein, we report a novel zeolite-catalyzed nucleophilic substitution in allyl alcohols. The product yield was improved upon the addition of NaOTf (0.05 mol%) using the studied zeolites. The highest yields were observed using H-*BEA(Si/Al_2=40)/NaOTf. The scope of the reaction with respect to the nucleophile was examined using 1,3-diphenylprop-2-ene-1-ol as a model substrate under optimized reaction conditions. *p*-Substituted aryl sulfonamides bearing electron-rich or electron-deficient substituents, alkyl sulfonamides, and heteroaryl sulfonamides undergo the amidation reaction to produce their corresponding allyl sulfonamides in good yield. Amides and anilines exhibited low activity under the optimized conditions, however, performing the reaction at 90 °C produced the target product. The scope of the allyl alcohol was investigated using *p*-toluenesulfonamide as the nucleophile and the reaction proceeded with a variety of allylic alcohols. To probe the practical utility of the H-*BEA-catalyzed amidation reaction, a gram-scale reaction was performed using 1.01 g (4.8 mmol) of allyl alcohol, which afforded the target product in 88% yield.

Introduction

Allyl amides and allyl amines are crucial structures and synthetic building blocks found in natural products, medicines, functional compounds, and other highly bioactive molecules. [1] Catalytic amidation, including the oxidative amidation and amination of allyl alcohols, which produce water as the only byproduct, are very important strategies used in green chemistry and industrial chemistry. [2] Recently, there has been a continuous development of these reaction protocols using various catalytic systems. In general, sulfonamides were initially used as the nucleophile in this type of reaction, and many methods to efficiently release the hydroxyl group of an allyl alcohol have been reported (Scheme 1). Metal-catalyzed amidation and amination reactions of allyl alcohols have been studied over the last 30 years. For example, Hayashi and Yanagi first reported Pd-phosphine-catalyzed asymmetric allylic amination in 1989, [3] and Lu and co-workers reported the use of $Pd(OAc)_2$ as a catalyst in 2000. [4] In addition, many metals, including transition metals, and non-transition metal complexes or salts such as Re, [5] Mo, [6] Bi, [7] Au, [8] Ag, [8c] Yb, [9] Fe, [10] Al, [11] Zn, [12] and V [13] have also been used as catalysts (Scheme 1a). Brønsted acids (such as sulfonic acid, [14] carboxylic acids, [15] and phosphotungstic acid [16]), Lewis acids (such as I_2 [17]), and chiral Brønsted acids [18] have also been used as catalysts (Scheme 1b). There are also reports that do not use an external catalyst system, but there are many restrictions to their use, [19] such as the need for specialized solvents or strong bases with low nucleophilicity (such as bis(trimethylsilyl)amine). Moreover, solid, metal, and acid catalysts supported on a carrier have also been developed (Scheme 1c). [20] The problem with such reported solid catalyst systems is that they are time consuming to make.

Zeolites are microporous crystalline aluminosilicates constructed from infinitely extending three-dimensional networks of silicate (SiO_4) and aluminate (AlO_4) linked via oxygen bridges, which exhibit structural stability and non-corrosive and non-toxic properties as well as similar properties to those observed for Brønsted acids. Solid catalysts, in which the metal complex is supported on a zeolite or using the zeolite itself as a solid acid catalyst, have been studied in many organic reactions. [21] The advantage of using the zeolite itself as a solid acid catalyst is that the isolation of the product is easier than when using a transition metal catalyst. Consequently, reuse of the catalyst is easy. Herein, we report a novel zeolite-catalyzed nucleophilic substitution in allyl alcohols using sulfonamides, amides, and amines (Scheme 1d). The catalyst system using our zeolite reported here is advantageous in that a commercial product can be directly used as a catalyst.



Scheme 1. Strategies for the substitution of the hydroxy group in allyl alcohols.

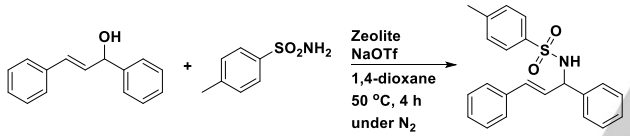
[a] Dr. Akimichi Ohtsuki, Mr. Shunsuke Aoki, Mr. Ryo Nishida, Ms. Sachiko Morita, Mr. Takeshi Fujii, Prof. Dr. Kazu Okumura
Applied Chemistry
Kogakuin University
2665-1 Nakano-cho, Hachioji, Tokyo 192-0015, Japan
http://www.ns.kogakuin.ac.jp/~wwb1019/
E-mail: kt13623@ns.kogakuin.ac.jp; okmr@cc.kogakuin.ac.jp

Supporting information for this article is given via a link at the end of the document.

Results and Discussion

Initially, we performed a typical amidation reaction using 1,3-diphenylprop-2-ene-1-ol (**1a**) and *p*-toluenesulfonamide (**2a**) in 1,4-dioxane at 50 °C for 4 h in the presence of different zeolite catalysts. The reaction occurred in all cases and Table 1 shows the extent of the reaction observed for the four zeolite catalysts studied (H-*BEA (Si/Al_2=40), entry 3; H-FAU (Si/Al_2=7), entry 5; H-MOR (Si/Al_2=18), entry 7; MFI (Si/Al_2=40), entry 9). When the reaction was carried out in the absence of the zeolite catalyst, the reaction did not occur (entry 1). Furthermore, the yield was greatly improved upon the addition of NaOTf (0.05 mol% for **1a**) when using any of the zeolite catalysts studied (entries 4, 6, 8, and 10). In particular, the highest yield was observed when using H-*BEA/NaOTf (96%, entry 4). However, almost no reaction was observed when using NaOTf alone (entry 2). From these results, we decided to use the H-*BEA/NaOTf catalyst system.

Table 1. The Zeolite-catalyzed allyl sulfoneamide formation from 1,3-diphenylprop-2-ene-1-ol (**1a**) and *p*-toluenesulfonamide (**2a**) [a]



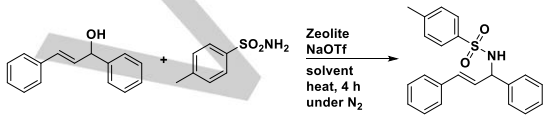
1a 2a 3aa

Entry	Catalyst (Si/Al_2)	NaOTf	NMR Yield (%) [b]
1	None	0 mol%	trace
2	None	0.05 mol%	8
3	H-*BEA (40)	0 mol%	25
4	H-*BEA (40)	0.05 mol%	96
5	H-FAU (7)	0 mol%	5
6	H-FAU (7)	0.05 mol%	33
7	H-MOR (18)	0 mol%	0
8	H-MOR (18)	0.05 mol%	84
9	H-MFI (40)	0 mol%	7
10	H-MFI (40)	0.05 mol%	77

[a] Reaction conditions: 0.48 mmol of 1,3-diphenylprop-2-ene-1-ol (**1a**) and 0.96 mmol of *p*-toluenesulfonamide (**2a**), Zeolite 21 mg, NaOTf 0 or 0.05 mol% (0 or 0.24 μmol), 0.5 mL 1,4-dioxane, under N_2 atmosphere. [b] This yield was determined by ^{1}H NMR.

Table 2 lists the results obtained during the initial screening study of the reaction conditions using H-*BEA as the catalyst. Upon comparing the catalytic activity of H-*BEA using different Si/Al_2 ratios, the product yield was increased upon the addition of NaOTf (entry 1–5). In particular, H-*BEA(Si/Al_2=40) and NaOTf (0.05 mol%) gave the highest yield (96%, entry 2). When the reaction temperature was investigated (entries 2 and 6–8), the strongest effect upon adding NaOTf was observed between 0 and 50 °C, but not at 90 °C. From these results, we decided to use 50 °C as the reaction temperature. We then confirmed the effect of the solvent on the reaction (entries 2 and 9–11). In each case, the effect of NaOTf was observed except for ethyl acetate and the optimum solvent was determined to be 1,4-dioxane. These surprising effects of small amount of NaOTf are currently unclear. We are thinking that the partial protonation of the nucleophiles under acidic conditions caused by zeolite was inhibited by changing the acid-base equilibrium by triflate anion. From the results, we decided to use the conditions in entry 2-right as the standard conditions for the amidation reaction.

Table 2. Optimizations of H-*BEA-zeolite and reaction conditions [a]



1a 2a 3aa

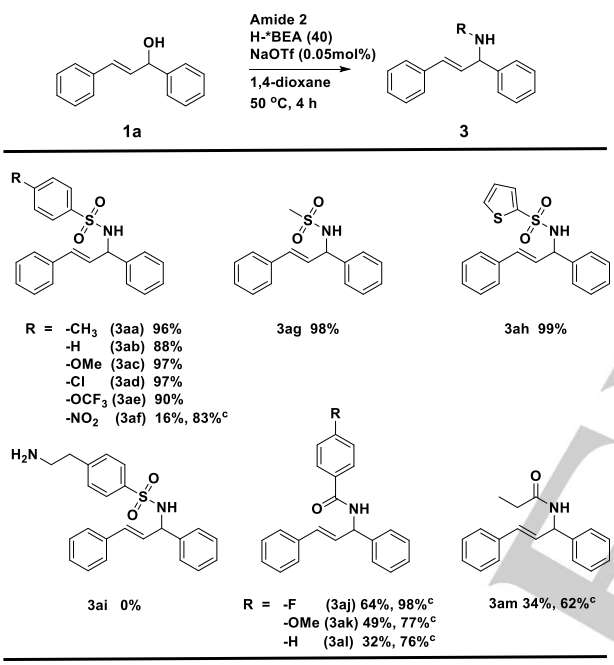
Entry	Zeolite (Si/Al_2)	solvent	Temp. (°C)	NMR Yield (%) [b]	
				No additive	NaOTf 0.05 mol%
1	None	1,4-dioxane	50	trace	8
2	H-*BEA (40)	1,4-dioxane	50	25	96
3	H-*BEA (18)	1,4-dioxane	50	26	39
4	H-*BEA (100)	1,4-dioxane	50	50	62
5	H-*BEA (500)	1,4-dioxane	50	30	49
6	H-*BEA (40)	1,4-dioxane	0	22	42
7	H-*BEA (40)	1,4-dioxane	r.t	30	61
8	H-*BEA (40)	1,4-dioxane	90	82	99
9	H-*BEA (40)	THF	50	25	71
10	H-*BEA (40)	toluene	50	82	99
11	H-*BEA (40)	ethyl acetate	50	91	91

[a] Reaction conditions: 0.48 mmol of 1,3-diphenylprop-2-ene-1-ol (**1a**) and 0.96 mmol of *p*-toluenesulfonamide (**2a**), Zeolite 21 mg, NaOTf 0 or 0.05 mol% (0 or 0.24 μmol), 0.5 mL 1,4-dioxane, under N_2 atmosphere. [b] This yield was determined by ^{1}H NMR.

The scope of the reaction with respect to the amide was examined using 1,3-diphenylprop-2-ene-1-ol (**1a**) as a model substrate under standard conditions (Table 3). In the case of *p*-substituted aryl sulfonamides **2a** and **2c**–**2f** bearing either electron-rich or electron-deficient substituents, the amidation reaction proceeded to give their corresponding allyl sulfonamides products (**3aa**–**3ae**) in good yield. Functional groups such as methoxy (**2c**), chloro (**2d**) trifluoromethoxy (**2e**), and nitro (**2f**) were retained under the standard reaction conditions. Alkyl sulfonamide **2g** and heteroaryl sulfonamide **2h** also participated in the reaction. *p*-Nitrophenylsulfonamide **2f** exhibited low activity toward allyl alcohol **1a** under the standard conditions. However, performing the reaction at 90 °C gave the desired allyl sulfonamide product (**3af**). This problem was easily overcome by changing the reaction conditions. When *p*-(aminoalkyl)benzene sulfonamide **2i** was used as the nucleophile, the reaction did not proceed under any of the reaction conditions studied. The new optimized conditions (90 °C, 4 h) were applied to the reactions using amides **2j**–**2m**. In

the case of the benzamide derivatives bearing electron-deficient (*p*-fluorobenzamide (**2j**)) or electron-rich (*p*-methoxyamide (**2k**)) substituents, the amidation reaction proceeded to give their corresponding allyl sulfonamide products (**3aj**–**3al**) in good yield. In addition to benzamides, alkylbenzamides (butyramide (**2m**)) also participated in the reaction under the new optimized conditions. Similarly, the scope of the reaction with respect to the aniline was examined using 1,3-diphenylprop-2-ene-1-ol (**1a**) as a model substrate (Table 4). The reaction did not proceed under the standard conditions.

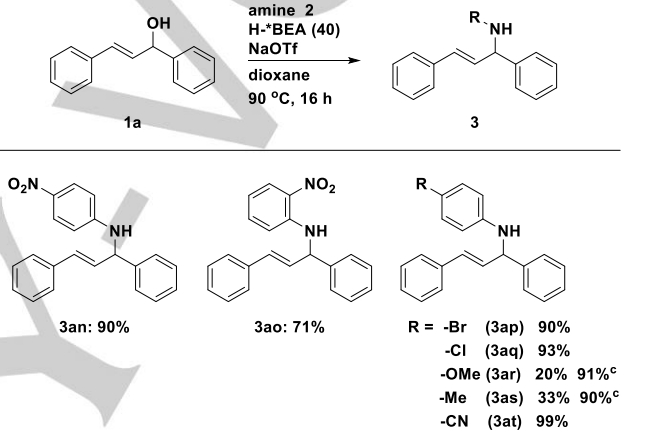
Table 3. Substrate scope in the amidation of 1,3-diphenylprop-2-ene-1-ol (**1a**) [a, b]



[a] Reaction conditions: 0.48 mmol of 1,3-diphenylprop-2-ene-1-ol (**1a**) and 0.96 mmol of amides (**2**), Zeolite 21 mg, NaOTf 0.05 mol%(0.24 μmol), 0.5 mL 1,4-dioxane, under N_2 atmosphere. [b] This yield was determined by ^{1}H NMR. [c] Reaction temperature was 90 °C, reaction time was 16 h.

The new optimized conditions (90 °C, 4 h) were applied to the reactions using anilines **2n–2s**. In the case of the *p*-substituted electron-deficient anilines (**2n**, **2p,** and **2q**), the amination reaction proceeded to give their corresponding allyl amine products (**3an**, **3ap,** and **3aq**) in moderate or good yield. Unfortunately, *o*-nitroaniline (**2o**) and electron-rich anilines **2r** and **2s** were found to be much less reactive under these conditions. However, this problem was easily overcome by changing the reaction solvent. By performing the reaction in toluene at 90 °C for 16 h, the catalytic amination with *o*-nitroaniline (**2o**) produced the target allyl amine product (**3ao**) in good yield (73%). The optimized new conditions were applied to anilines **2r** and **2s** and the corresponding allyl amine products (**3ar** and **3as**) were obtained in high yield. Subsequently, the scope of the allyl alcohols used in the reaction was investigated using *p*-toluenesulfonamide (**2a**) as the nucleophile (Table 5). The catalytic amidation reactions of electron-deficient (**1b**) and electron-rich (**1c**) substrates proceeded in high yield. However, α-methylated allyl alcohol **2d** did not show any reactivity toward allyl alcohol **1a** under standard conditions and the reaction was performed at 90 °C for 4 h. The amidation of 4-phenyl-3-butene-2-ol (**1e**) also afforded allyl sulfonamides **3ea** and **3fa** in 43% and 4% yield, respectively under the standard conditions. However, upon heating at 90 °C for 4 h, the amidation reaction

Table 4. Substrate scope in the amination of 1,3-diphenylprop-2-ene-1-ol (**1a**) [a, b]



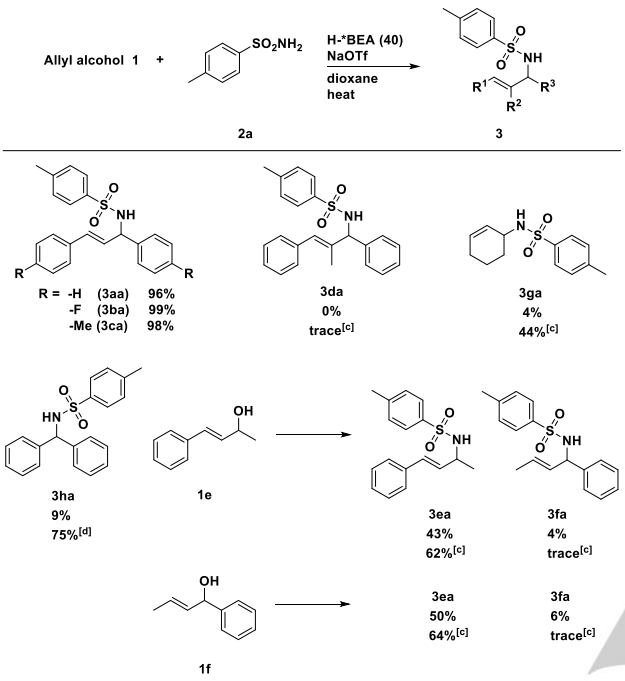
[a] Reaction conditions : 0.48 mmol of 1,3-diphenylprop-2-ene-1-ol (**1a**) and 0.96 mmol of anilines (**2**), H-*BEA 21 mg, NaOTf 0.05 mol% (0.24 μmol), 0.5 mL 1,4-dioxane, under N_2 atmosphere. [b] This yield was determined by ^{1}H NMR. [c] Solvent was changed to toluene (0.5 mL).

of **1e** proceeded with allyl sulfonamides **3ea** and **3fa** to give their corresponding products in 62% and 0%, respectively. The amidation of 1-phenylbut-2-en-1-ol (**1f**) was preceded with allyl sulfonamides **3ea** and **3fa** in 50%zs and 6% yield, respectively under the standard conditions. When heated at 90 °C for 4 h, the amidation reaction of **1e** proceeded with allyl sulfonamides **3ea** and **3fa** in 64% and 0%, respectively. In addition, cyclic allylic alcohol **1g**, which had no aromatic ring in its structure, did not show any reactivity under the standard conditions, but a 44% yield of **3ga** was obtained upon heating at 90 °C for 16 h. Similarly, diphenylmethanol (**1h**), which is not an allyl alcohol, gave the target product (**3ha**) in low yield under standard conditions, but in 67% yield upon heating at 90 °C for 16 h.

Typically, alcohols can act as nucleophiles in the reaction and produce dimeric ethers under acidic conditions. To examine whether dimeric ether (**4aa**) was involved in the reaction mechanism of this catalytic amidation, the reaction was investigated using ether **4aa** as a substrate instead of allyl alcohol **1a** (Scheme 2). Ether **4aa** (0.24 mmol) and *p*-toluenesulfonamide **2a** (0.96 mmol) were reacted to produce a 93% NMR yield of allylamide under the standard conditions. This result suggests the existence of a catalytic amidation reaction

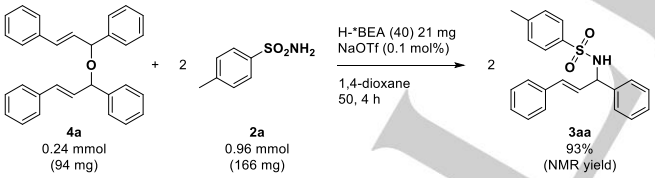
mechanism involving ether **4aa** after catalytic ether formation via a protonated allyl alcohol intermediate from allyl alcohol **1a**. [22]

Table 5. Substrate scope in the amidation of allyalcohols (**1**) with *p*-toluenesulfonamide (**2a**) [a, b]



[a] Reaction conditions : 0.48 mmol of allylalcohols (**1**) and 0.96 mmol of *p*-toluenesulfonamide (**2a**), Zeolite 21 mg, NaOTf 0.05 mol% (0.24 μmol), 0.5 mL 1,4-dioxane, under N_2 atmosphere. [b] This yield was determined by ^{1}H NMR. [c] Reaction temperature was 90 °C, reaction time was 4 h. [d] Reaction temperature was 90 °C, reaction time was 16 h.

Scheme 2. Catalytic amidation of dimeric ether (**4aa**)

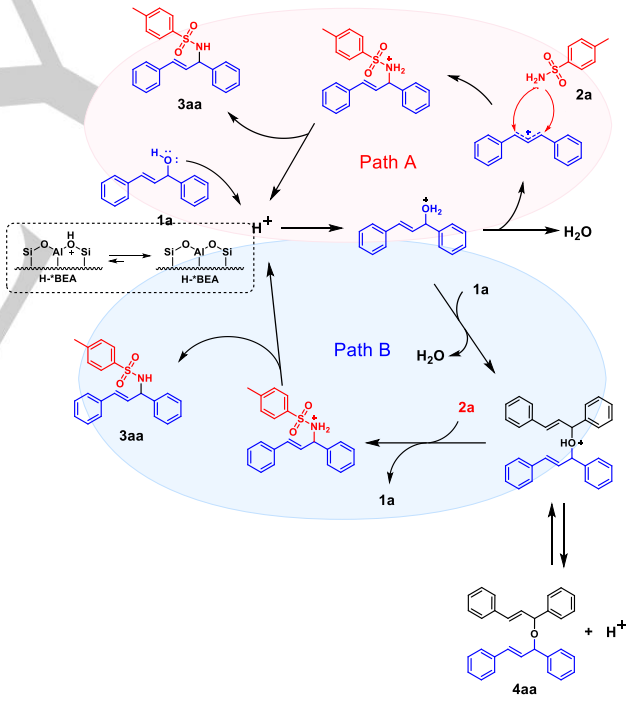


Based on the above experimental results and previously reported acid catalysts, we proposed a mechanism for the reaction, as shown in Scheme 3. Initially, the proton released in the catalytic cycle from the acid site of H-*BEA is coordinated to the hydroxyl group of the allyl alcohol and water is then eliminated to form an allyl-cation intermediate. A nucleophile attacks on the allyl cation from the less sterically hindered side followed by deprotonation gives the target allyl amide (Path A). Similarly, the protonated allyl alcohol may react with a non-protonated allyl alcohol to form a protonated dimeric ether. The protonated dimeric ether can undergo nucleophilic attack at the carbon atom followed by deprotonation to give the target allyl amide product (Path B). Unfortunately, the mechanism of increasing the catalyst activity by NaOTf is not clearly understood, but we propose that NaOTf is involved in the release of protons from the zeolite catalyst. We will conduct this analysis in our future work.

To further probe the practical utility of the H-*BEA-catalyzed amidation reaction, a gram-scale reaction was conducted using 1.01 g (4.8 mmol) of **1a** to obtain allyl amide **3aa** in 88% yield under the standard conditions (*See Experimental section*).

The reaction between **1a** and **2a** was performed over H-*BEA with varied Al concentration. The acid amount of these H-*BEA was measured with temperature programmed desorption of NH_3 and the data was summarized in Table S2. The yield of allyl amide **3aa** was dependent on the Al concentration (Al/(Si+Al)) of H-*BEA; the highest yield was obtained with the use of H-*BEA with Al/(Si+Al)=0.012 (Si/Al_2=40) as shown in Figure S1. On further increase in the Al concentration, the yield decreased. The tendency was rather unexpected because Brønsted acid sites located at the external surface of H-*BEA was supposed to be the active sites for reaction. Probably, the adsorbed water, the amount of which is higher in with high-Al zeolite, hindered the formation of allyl-cation intermediate in Scheme 3.

Scheme 3. Proposal mechanism



Conclusion

We developed a novel H-*BEA zeolite-catalyzed nucleophilic substitution of allyl alcohols using a variety of nitrogen nucleophiles. This catalytic system was activated upon the addition of a very small amount of NaOTf and could be applied to a wide range of nucleophiles. Furthermore, the synthetic utility of this H-*BEA zeolite nucleophilic substitution

protocol has been demonstrated using a gram-scale reaction. Studies on the reaction mechanism, synthetic versatility, application of this practical catalytic system to other acid catalyst reactions, and the role of NaOTf in the catalytic system are now in progress.

Experimental Section

Analytical thinlayer chromatography (TLC) was performed on silica gel 60 F_{254} plates (Millipore). ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on a JEOL ECZ-400 spectrometer (JEOL) in $CDCl_3$ or DMSO-d_6 using tetramethylsilane (TMS) as an internal reference standard. The NMR chemical shifts are reffered singnals of $CDCl_3$ (δ_H 7.27 ppm) and DMSO-d_6 (δ_H 2.50 ppm) for ^{1}H, and to the central line of $CDCl_3$ (δ_C 77.16 ppm) and DMSO-d_6 (39.52 ppm) for ^{13}C. NMR data have been reported as follows: chemical shifts (δ) in ppm , multiplicity (*s* = singlet, *d* = doublet, *t* = triplet, *q* = quartet and *m* = multiplet), coupling constant (*J*) in Hz, and integration. High resolution mass spectra (HRMS) were obtained on a JEOL JMS-GC MATEII GCMS system. The Fourier transform Infrared (FT-IR) spectra were recorded as KBr pallets on Spectrum One (Perkin Elmer Precisely) by using potassium bromide disks and monitored in 4000 - 1000 cm^{-1} region. The IR absorptions have been reported in reciprocal centimeters with the following relative intensities: s (strong), m (medium), or w (weak). Melting points (Mp.) were measured on a Yanagimoto MP-S3 micro melting point apparatus (Yanagimoto), differential thermal analyzer and are uncorrected. Column chromatography was performed with Silica Gel 60 (spherical, neutral) (63-210 μm, KANTO Chemical). Medium-pressure column chromatography was carried out on a Biotage Flash Purification System Isolera (Biotage), equipped with a 254 nm UV detector.

All commercial reagents and dry solvents were used without futher purification. All reactions were carried out under N_2 atmosphere. 1,4-dioxane, ethyl acetate, toluene, methanol and ethanol (for solvent) were purchased from KANTO Chemical and used as received. Tetrahydrofuran (for solvent) was purchased from WAKO Chemicals and used as received. All zeolites were purchased from TOSOH Inc.. Ally alcohols, trans-1, 3-diphenyl-2-propen-1-ol **1a** (TCI), 2-cyclohexen-1-ol **1g** (Aldrich) and benzhydrol **1h** (TCI), were purchased from the specified commercial suppliers and used as received. 4-Fluoro-α-[(1*E*)-2-(4-fluorophenyl)ethenyl]-benzenemethanol **1b**, [23] 4-Methyl-α-[(1*E*)-2-(4-methylphenyl)ethenyl]-benzenemethanol **1c**, [24] α-[(1*E*)-1-methyl-2-phenylethenyl]-benzenemethanol **1d**, [25] 4-phenyl-3-buten-2-ol **1e,** [26] and α-1-propen-1-yl-benzenemethanol **1f** [27] were prepared according to the literature procedures. [Oxybis(prop-1-ene-3,1,3-triyl)]tetrabenzene **4aa** was prepared using original procedure. All sulfonamides, *p*-toluenesulfonamide **2a** (TCI), benzenesulfonamide **2b** (TCI), 4-methoxybenzenesulfonamide **2c** (Aldrich), 4-chlorobenzenesulfonamide **2d** (TCI), 4-(trifluoromethoxy) benzenesulfonamide **2e** (TCI), 4-nitrobenzenesulfonamide **2f** (TCI), methanesulfonamide **2g** (TCI), 2-thiophenesulfonamide **2h** (TCI) and 4-(2-aminoethyl)benzenesulfonamide **2i** (Wako), were purchased from the specified commercial suppliers and used as received. All amides, 4-fluorobenzamide **2j** (TCI), 4-methoxybenzamide **2k** (TCI), benzamide **2l** (TCI) and propylamide **2m** (TCI), were purchased from the specified commercial suppliers and used as received. All anilines, 4-nitroaniline **2n** (Wako), 2-nitroaniline **2o** (TCI), 4-bromoaniline **2p** (TCI), 4-chloroaniline **2q** (TCI), 4-methoxyaniline **2r** (TCI), 4-methylaniline **2s** (Wako) and 4-aminobenzonitrile **2t** (Wako), were purchased from the specified commercial suppliers and used as received. Sodium trifluoromethansulfonate (TCI) was purchased from the specified commercial suppliers and used as received.

Synthesis of Ally Alcohols and Ethers

4-Fluoro-α-[(1*E*)-2-(4-fluorophenyl)ethenyl]-benzenemethanol (1b)

Chang's protocol used. [23] 1,3-Bis(4-fluorophenyl)-(2*E*)-2-propen-1-one (1.02 g, 4.18 mmol), dry-methanol (20 mL) and dry THF (20 mL) were added to a 100 mL flask with stir bar under N_2 atmosphere, and the solution was stirred and cooled to 0 °C. Then, $NaBH_4$ (1.04 g, 27.5 mmol) was added to the reaction flask and the reaction mixture was warmed to room temperature and stirred for 1 h. The reaction was monitored using TLC. After reaction, the reaction flask was cooled to 0 °C and saturated aqueous solution of NH_4Cl (200 mL) was slowly added to quenching of $NaBH_4$. The mixture was partitioned between ethyl acetate and saturated aqueous solution of NH_4Cl. The organic layer was washed with saturated aqueous solution of NH_4Cl and water, dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by column chromatography on neutral silica gel (20 - 30% ethyl acetate / hexane) to give a title compound as colorless viscous oil (911 mg, 89%). R_f = 0.37 (40% ethyl acetate/hexane). ^{1}H NMR ($CDCl_3$, 400 MHz): 7.39-7.32 (*m*, 4 H), 7.08-6.98 (*m*, 4 H), 6.62 (*d*, *J* = 16.0 Hz, 1 H), 6.26 (*dd*, *J* = 16.0, 6.40 Hz, 1 H), 5.34 (*d*, *J* = 6.40 Hz, 1 H), 2.34 (*brs*, 1 H). ^{13}C NMR ($CDCl_3$, 100 MHz): 163.8 (*d*, $J_{C\text{-}F}$ =13.4 Hz), 161.3 (*d*, $J_{C\text{-}F}$ = 12.5 Hz), 138.5 (*d*, $J_{C\text{-}F}$ = 2.8 Hz), 132.6 (*d*, $J_{C\text{-}F}$ = 3.8 Hz), 131.1, 129.7, 128.3 (*d*, $J_{C\text{-}F}$ = 7.7 Hz), 128.2 (*d*, $J_{C\text{-}F}$ = 8.6 Hz), 115.7 (*d*, $J_{C\text{-}F}$ = 8.6 Hz), 115.5 (*d*, $J_{C\text{-}F}$ = 7.7 Hz), 74.5.

4-Methyl-α-[(1*E*)-2-(4-methylphenyl)ethenyl]-benzenemethanol (1c)

Umeda's protocol used. [24] The solution of 4-methylbenzaldehyde (1.01 g, 8.39 mmol) and 1-(4-methylphenyl)ethanone (1.21 g, 9.02 mmol) in ethanol (20 mL) was added to a 300 mL flask with stir bar, and the solution was stirred and cooled to 0 °C. Then, H_2O(10 mL) and KOH (521 mg, 9.30 mmol) were added to the reaction flask and the reaction mixture was warmed to room temperature and stirred for overnight. This reaction was monitored using TLC. After reaction, H_2O (200 mL) was added to the reaction flask, and the mixture

was partitioned between ethyl acetate and water. The organic layer was washed with water, dried (Na_2SO_4) and concentrated *in vacuo* to give 1,3-bis(4-methylphenyl)-(2*E*)-2-Propen-1-one (**1cc**) as yellow viscose oil. This compound was used for the subsequent reaction without further purification. R_f = 0.30 (30% ethyl acetate/hexane). ^{1}H NMR ($CDCl_3$, 400 MHz): 7.93 (*d*, *J* = 8.40 Hz, 2 H), 7.79 (*d*, *J* = 16.0 Hz, 1 H), 7.56-7.47 (*m*, 2 H), 7.30 (*d*, *J* = 8.00 Hz, 2 H), 7.23 (*d*, *J* = 8.00 Hz, 2 H), 2.44 (*s*, 3 H), 2.40 (*s*, 3 H). ^{13}C NMR ($CDCl_3$, 100 MHz): 190.3, 144.6, 143.6, 141.1, 135.9, 132.4, 129.8, 129.4, 128.8, 128.6, 121.2, 21.8, 21.7.

The residue (1,3-bis(4-methylphenyl)-(2*E*)-2-propen-1-one, 95% NMR purity) methanol (20 mL) and THF (20 mL) were added to a 300 mL flask with stir bar under N_2 atmosphere, and the reaction flask was stirred and cooled to 0 °C. Then, $NaBH_4$ (412 mg, 10.9 mmol) was added to the reaction flask and the reaction mixture was warmed to room temperature and stirred for overnight. The reaction was monitored using TLC. After reaction, the reaction flask was cooled to 0 °C and saturated aqueous solution of NH_4Cl (200 mL) was slowly added to quenching of $NaBH_4$. The mixture was partitioned between ethyl acetate and saturated aqueous solution of NH_4Cl. The organic layer was washed with saturated aqueous solution of NH_4Cl and water, dried (Na_2SO_4) and concentrated in vacuo. The residue was purified by column chromatography on neutral silica gel (10 - 20% ethyl acetate / hexane) to give a title compound as white solid (1.62 g, 90% (two steps)). R_f = 0.47 (40% ethyl acetate/hexane). ^{1}H NMR ($CDCl_3$, 400 MHz): 7.37-7.31 (*m*, 2 H), 7.24-7.21 (*m*, 2 H), 7.18-7.14 (*m*, 2 H), 6.67 (*d*, *J* = 16.0 Hz, 1 H), 6.37 (*dd*, *J* = 16.0, 6.60 Hz, 1 H), 5.35 (*d*, *J* = 6.60 Hz, 1 H), 2.46 (*brs*, 1 H), 2.41 (*s*, 3 H), 2.39 (*s*, 3 H). ^{13}C NMR ($CDCl_3$, 100 MHz): 140.1, 137.6, 137.5, 133.9, 130.8, 130.3, 129.3, 126.6, 126.4, 75.0, 21.3, 21.2.

α-[(1E)-1-methyl-2-phenylethenyl]-benzenemethanol (1d)

The precursor was prepared using Yangr's method. [25] Benzaldehyde (1.04 g, 9.80 mmol), 1-phenyl-1-propanone (1.40 g, 10.1 mmol), piperidine (2.0 mL, 1.72 g, 20.2 mmol), acetic acid (2.0 mL, 2.1 g, 35.0 mmol) and ethanol (10 mL) were added to 100 mL flask with stir bar and reflux condenser. The reaction mixture was stirred at 85 °C for 13 h. This reaction was monitored using TLC and ^{1}H NMR. To this reaction mixture, saturated aqueous solution of NH_4Cl (100 mL) was slowly added to quenching the reaction. The mixture was partitioned between ethyl acetate and saturated aqueous solution of NH_4Cl. The organic layer was washed with water, dried (Na_2SO_4) and concentrated in vacuo to give (*E*)-2-methyl-1,3-diphenylprop-2-en-1-one as viscose yellow oil (NMR purity was 50%). This compound was used for the subsequent reaction without further purification. R_f = 0.30 (30% ethyl acetate/hexane).

The residue ((*E*)-2-methyl-1,3-diphenylprop-2-en-1-one, 50% NMR purity), methanol (20 mL) and THF (20 mL) were added to a 300 mL flask with stir bar under N_2 atmosphere, and the reaction flask was stirred and cooled to 0 °C. Then, $NaBH_4$ (825 mg, 29.6 mmol) was added to the reaction flask and the reaction mixture was warmed to room temperature and stirred for 2 h. The reaction was monitored using TLC. After reaction, the reaction flask was cooled to 0 °C and saturated aqueous solution of NH_4Cl (100 mL) was slowly added to quenching of $NaBH_4$. The mixture was partitioned between ethyl acetate and saturated aqueous solution of NH_4Cl. The organic layer was washed with saturated aqueous solution of NH_4Cl and water, dried (Na_2SO_4) and concentrated in vacuo. The residue was purified by column chromatography on neutral silica gel (0 - 20% ethyl acetate / hexane) to give a title compound as white solid (1.22 g, 55% (two steps)). R_f = 0.48 (40% ethyl acetate/hexane). ^{1}H NMR ($CDCl_3$, 400 MHz): 7.47-7.44 (*m*, 2 H), 7.41-7.30 (*m*, 7 H), 7.28-7.22 (*m*, 1 H), 6.80 (*s*, 1 H), 5.30-5.29 (*m*, 1 H), 2.11-2.10 (*m*, 1 H), 1.76-1.76 (*m*, 3 H). ^{13}C NMR ($CDCl_3$, 100 MHz): 142.2, 139.7, 137.6, 129.2, 128.5, 128.3, 127.7, 126.7, 126.6, 126.1, 79.6, 14.2.

4-phenyl-3-buten-2-ol (1e)

Onaka's protocol used. [26] 4-Phenyl-3-buten-2-one (1.18 g, 8.07 mmol) and dry-methanol (100 mL) were added to a 300 mL flask with stir bar under N_2 atmosphere, and the solution was stirred and cooled to 0 °C. Then, $NaBH_4$ (372 mg, 9.84 mmol) was added to the reaction flask and the reaction mixture was warmed to room temperature and stirred for 1 h. The reaction was monitored using TLC. After reaction, the reaction flask was cooled to 0 °C and aqueous solution of HCl (0.2 M, 20 mL) was slowly added to quenching of $NaBH_4$ and water (80 mL) was added. The mixture was partitioned between ethyl acetate and water. The organic layer was washed with HCl aq (0.2 M) and water, dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by column chromatography on neutral silica gel (30% ethyl acetate / hexane) to give a title compound as colorless oil (1.01 g, 85%). R_f = 0.34 (40% ethyl acetate/hexane). ^{1}H NMR ($CDCl_3$, 400 MHz): 7.40-7.23 (*m*, 5 H), 6.57 (*d*, *J* = 16.0 Hz, 1 H), 6.27 (*dd*, *J* = 16.0, 6.60 Hz, 1 H), 4.50-4.47 (*m*, 1 H), 2.31 (*brs*, 1 H), 1.39 (*d*, *J* = 6.40 Hz, 3 H). ^{13}C NMR ($CDCl_3$, 100 MHz): 136.8, 133.7, 129.4, 128.6, 127.7, 126.5, 68.9, 23.5.

***α*-1-propen-1-yl-benzenemethanol (1f)**

Nau's protocol used. [27] 2-Butenal (1.05 g, 14.9 mmol) and dry THF (50 mL) were added to a 300 mL flask with stir bar under N_2 atmosphere, and the solution was stirred and cooled to 0 °C. The solution of phenylmagnesium bromide in diethyl ether (3.0 M solution, 7 mL, 21 mmol) was slowly added to the reaction flask and the reaction mixture was warmed to room temperature and stirred for 1 h. This reaction was monitored using TLC. After reaction, the reaction flask was cooled to 0 °C and saturated aqueous solution of NH_4Cl (100 mL) was slowly added to quenching of phenylmagunesium bromide. The mixture was partitioned between ethyl acetate and saturated aqueous solution of NH_4Cl. The organic layer was washed with saturated aqueous solution of NH_4Cl and water, dried (Na_2SO_4) and

concentrated in vacuo. The residue was purified by column chromatography on neutral silica gel (0 – 30% ethyl acetate / hexane) to give a title compound as colorless oil (1.83 g, 83%). R_f = 0.65 (40% ethyl acetate/hexane). ^{1}H NMR ($CDCl_3$, 400 MHz): 7.40-7.29 (*m*, 5 H), 5.79-5.67 (*m*, 2 H), 5.13 (*d*, *J* = 5.60 Hz, 1H), 2.83 (*brs*, 1 H), 1.75 (*d*, *J* = 6.00 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 100 MHz): 143.4, 133.7, 128.4, 127.4, 127.2, 126.2, 75.0, 17.7.

[Oxybis(prop-1-ene-3,1,3-triyl)]tetrabenzene (4aa) [28]

trans-1,3-Diphenyl-2-propen-1-ol **1a** (1.01 g, 4.79 mmol), *p*-toluenesulfonamide **2a** (1.60 g, 9.37 mmol), Ion Exchange Resin (Amberlyst 15E, 8.8 mg), toluene (5 mL) and stir bar were added to a 30 mL-sample vial with a Teflon-sealed screwcap. The reaction mixture was stirred at 50 °C for 4 h under nitrogen atmosphere. After reaction, H-*BEA was removed by filtration and the result solution was concentrated in vacuo. The residue was purified by Flash column chromatography on neutral silica gel (0–5% ethyl acetate / hexane) to give compound **4aa** as colorless viscose oil (740 mg, 77%). R_f = 0.51 (40% ethyl acetate/hexane). ^{1}H NMR ($CDCl_3$, 400 MHz): 7.45-7.20 (*m*, 20 H), 6.61 (*dd*, *J* = 16.0, 4.00 Hz, 2 H), 6.41-6.30 (*m*, 2 H), 5.11 (*t*, *J* = 7.40 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 100 MHz): 141.4, 141.3, 136.7, 131.7, 131.5, 130.6, 130.4, 128.7, 127.8, 127.2, 126.7, 126.5, 79.3, 79.2.

Typical Procedure for H-*BEA Zeolite Catalyzed Substitution of Allyl Alcohols

1. Procedure for H-*BEA zeolite catalyzed substitution of allyl alcohol 1a with sulfonamides

Allyl alcohol **1a** (100 mg, 0.48 mmol), sulfonamide **2** (0.96 mmol), H-*BEA (Si/Al_2 = 40, 21 mg), 1,4-dioxane (500 μL) and stir bar were added to a 10 mL-sample vial with a Teflon-sealed screwcap. Then, a solution of NaOTf in 1, 4-dioxane (14.5 mM, 17 μL, about 0.0246 μmol) was added to the reaction mixture and stirred at 50 or 90 °C for 4 h under nitrogen atmosphere. After reaction, H-*BEA was removed by short column (ethyl acetate, neutral silica gel) and the result solution was concentrated in vacuo. 3,4,5-Trichloropyridine was added as an internal standard, and ^{1}H NMR analysis was performed to determine a NMR yield.

2. Procedure for H-*BEA zeolite catalyzed substitution of allyl alcohol 1a with amides

Allyl alcohol **1a** (100 mg, 0.48 mmol), amide **2** (0.96 mmol), H-*BEA (Si/Al_2 = 40, 21 mg), 1,4-dioxane (500 μL) and stir bar were added to a 10 mL-sample vial with a Teflon-sealed screwcap. Then, a solution of NaOTf in 1, 4-dioxane (14.5 mM, 17 μL, about 0.0246 μmol) was added to the reaction mixture and stirred at 50 or 90 °C for 4 h under nitrogen atmosphere. After reaction, H-*BEA was removed by short column (ethyl acetate, neutral silica gel) and the result solution was concentrated in vacuo. 3,4,5-Trichloropyridine was added as an internal standard, and ^{1}H NMR analysis was performed to determine a NMR yield.

3. Procedure for H-*BEA zeolite catalyzed substitution of allyl alcohol 1a with anilines in 1, 4-dioxane at 90 °C

Allyl alcohol **1a** (100 mg, 0.48 mmol), aniline **2** (0.96 mmol), H-*BEA (Si/Al_2 = 40, 21 mg), 1,4-dioxane (500 μL) and stir bar were added to a 10 mL-sample vial with a Teflon-sealed screwcap. Then, a solution of NaOTf in 1, 4-dioxane (14.5 mM, 17 μL, about 0.0246 μmol) was added to the reaction mixture and stirred at 90 °C for 16 h under nitrogen atmosphere. After reaction, H-*BEA was removed by short column (ethyl acetate, neutral silica gel) and the result solution was concentrated in vacuo. 3,4,5-Trichloropyridine was added as an internal standard, and ^{1}H NMR analysis was performed to determine a NMR yield.

4. Procedure for H-*BEA zeolite catalyzed substitution of allyl alcohol 1a with anilines in toluene at 110 °C

Allyl alcohol **1a** (100 mg, 0.48 mmol), aniline **2** (0.96 mmol), H-*BEA (Si/Al_2 = 40, 21 mg), toluene (500 μL) and stir bar were added to a 10 mL-sample vial with a Teflon-sealed screwcap. Then, a solution of NaOTf in toluene (14.5 mM, 17 μL, about 0.0246 μmol) was added to the reaction mixture and stirred at 110 °C for 16 h under nitrogen atmosphere. After reaction, H-*BEA was removed by short column (ethyl acetate, neutral silica gel) and the result solution was concentrated in vacuo. 3,4,5-Trichloropyridine was added as an internal standard, and ^{1}H NMR analysis was performed to determine a NMR yield.

5. Procedure for H-*BEA zeolite catalyzed substitution of allyl alcohols 1 with p-toluenesulfonamide 2a

Allyl alcohols **1** (0.48 mmol), *p*-toluenesulfonamide **2a** (166 mg, 0.96 mmol), H-*BEA (Si/Al_2 = 40, 21 mg), 1,4-dioxane (500 μL) and stir bar were added to a 10 mL-sample vial with a Teflon-sealed screwcap. Then, a solution of NaOTf in 1, 4-dioxane (14.5 mM, 17 μL, about 0.0246 μmol) was added to the reaction mixture and stirred at 90 °C for 16 h under nitrogen atmosphere. After reaction, H-*BEA was removed by short column (ethyl acetate, neutral silica gel) and the result solution was concentrated in vacuo. 3,4,5-Trichloropyridine was added as an internal standard, and ^{1}H NMR analysis was performed to determine a NMR yield.

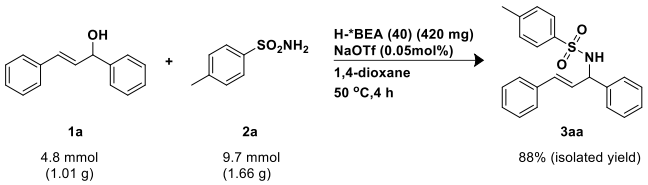
6. Procedure for H-*BEA zeolite catalyzed substitution of ether 4aa with p-toluenesulfonamide 2a

Ether **4aa** (94 mg, 0.24 mmol), *p*-toluenesulfonamide **2a** (166 mg, 0.96 mmol), H-*BEA (Si/Al_2 = 40, 21 mg), 1,4-dioxane (500 μL) and stir bar were added to a 10 mL-sample vial with a Teflon-sealed screwcap. Then, a solution of NaOTf in 1, 4-dioxane (14.5 mM, 17 μL, about 0.0246 μmol) was added to the

reaction mixture and stirred at 50 °C for 4 h under nitrogen atmosphere. After reaction, H-*BEA was removed by short column (ethyl acetate, neutral silica gel) and the result solution was concentrated in vacuo. 3,4,5-Trichloropyridine was added as an internal standard, and ^{1}H NMR analysis was performed to determine a NMR yield.

7. *Procedure for H-*BEA zeolite catalyzed substitution of allyl alcohol 1a with sulfonamides* 2a (A Gram-Scale)

Scheme 4. A gram schale reaction



trans-1,3-Diphenyl-2-propen-1-ol **1a** (1.01 g, 4.80 mmol), *p*-toluenesulfonamide **2a** (1.66 g, 9.70 mmol), H-*BEA (Si/Al$_2$ = 40, 420 mg) 1, 4-dioxane (5.0 mL) and stir bar were added to a 30 mL-sample vial with a Teflon-sealed screwcap. Then, a solution of NaOTf in 1, 4-dioxane (14.5 mM, 166 μL, about 0.24 μmol) was added to the reaction mixture and stirred at 50 °C for 4 h under nitrogen atmosphere. After reaction, H-*BEA was removed by short column (ethyl acetate, neutral silica gel) and the result solution was concentrated in vacuo. The residue was purified by column chromatography on neutral silica gel (0 - 20% ethyl acetate / hexane) to give compound **3aa** as white solid (1.53 g, 88%).

Spectroscopic Data of Products

N-[(2*E*)-1,3-diphenyl-2-propen-1-yl]-4-methylbenzenesulfonamide (3aa) [6a]

R_f = 0.51(40% ethyl acetate/hexane). White solid. ^{1}H NMR ($CDCl_3$, 400 MHz): 7.66 (*d*, *J* = 8.40 Hz, 2 H), 7.29-7.13 (*m*, 12 H), 6.35 (*d*, *J* = 16.0 Hz, 1 H), 6.08 (*dd*, *J* = 16.0, 6.80 Hz, 1 H), 5.12 (*t*, *J* = 6.80 Hz, 1 H), 5.03-5.01 (*m*, 1 H), 2.33 (*s*, 3 H). ^{13}C NMR ($CDCl_3$, 100 MHz): 143.4, 139.8, 137.9, 136.2, 132.3, 129.6, 128.9, 128.6, 128.3, 128.2, 128.0, 127.5, 127.2, 126.7, 59.9, 21.6. HRMS (EI) Calcd for $C_{22}H_{21}O_2NS$ 363.1293, Found 363.1289. FT-IR(KBr, cm^{-1}): 3298 s, 3029 w, 1599 m, 1494 m, 1451 m, 1429 m, 1339 m, 1322 s, 1303 m, 1290 m, 1162 s, 1151 s, 1092 m, 1019 m.

N-[(2*E*)-1,3-diphenyl-2-propen-1-yl]-benzenesulfonamide (3ab) [29]

R_f = 0.45 (40% ethyl acetate/hexane). White solid. ^{1}H NMR ($CDCl_3$, 400 MHz): 7.77 (*d*, *J* = 7.20 Hz, 2 H), 7.41 (*t*, *J* = 7.60 Hz, 1 H), 7.34 (*t*, *J* = 7.60 Hz, 2 H), 7.28–7.16(*m*, 10 H), 6.38 (*d*, *J* = 16.0 Hz, 1 H), 6.11 (*dd*, *J* = 16.0, 6.8 Hz, 1 H), 5.25-5.12 (*m*, 2 H). ^{13}C NMR ($CDCl_3$, 100 MHz): 140.9, 139.6, 136.1, 132.5, 132.3, 129.0, 128.9, 128.6, 128.3, 128.07, 128.05, 127.3, 128.2, 126.7, 59.9. HRMS (EI) Calcd for $C_{21}H_{19}O_2NS$ 349.1136, Found 349.1151. FT-IR(KBr, cm^{-1}): 3302 m, 3079 m, 3064 m, 3027 m, 1495 s, 1477 m, 1456 s, 1448 s, 1429 s, 1332 s, 1262 m, 1163 s, 1029 s, 1021 s.

N-[(2*E*)-1,3-diphenyl-2-propen-1-yl]-4-methoxy-benzenesulfonamide (3ac) [8c]

R_f = 0.43 (40% ethyl acetate/hexane). White solid. ^{1}H NMR ($CDCl_3$, 400 MHz): 7.72 (*d*, *J* = 9.20 Hz, 2 H), 7.29-7.17 (*m*, 10 H), 6.77 (*d*, *J* = 9.20 Hz, 2 H), 6.36 (*d*, *J* = 16.0 Hz, 1 H), 6.10 (*dd*, *J* = 16.0, 6.80 Hz, 1 H), 5.66 (*d*, *J* = 8.00 Hz), 5.12 (*t*, *J* = 7.20 Hz, 1 H), 3.72 (*s*, 3 H). ^{13}C NMR($CDCl_3$, 100 MHz); 162.7, 139.8, 136.2, 132.3, 132.0, 129.4, 128.7, 128.5, 128.3, 127.9, 127.8, 127.1, 126.6, 114.0, 59.8, 55.5. HRMS (EI) Calcd for $C_{22}H_{21}O_3NS$ 379.1242, Found 379.1243. FT-IR(KBr, cm^{-1}): 3350 m, 3082 m, 3053 m, 3032 m, 2909 w, 1633 s, 1601 s, 1578 s, 1521 s, 1488 s, 1455 m, 1363 m, 1312 s, 1250 m, 1205 m, 1143 m, 1073 m, 1042 m, 1022 m.

N-[(2*E*)-1,3-diphenyl-2-propen-1-yl]-4-chloro-benzenesulfonamide (3ad)

R_f = 0.52 (40% ethyl acetate/hexane). White needle crystal. Mp: 115-116 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): 7.66 (*d*, *J* = 8.80 Hz, 2 H), 7.30-7.15 (*m*, 12 H), 6.39 (*d*, *J* = 16.0 Hz, 1 H), 6.10 (*dd*, *J* = 16.0, 6.8 Hz, 1 H), 5.16 (*t*, *J* = 7.0 Hz, 1 H), 5.09-5.07 (*m*, 1 H). ^{13}C NMR ($CDCl_3$, 100 MHz): 139.5, 139.3, 139.1, 135.9, 132.7, 129.2, 129.0, 128.8, 128.7, 128.3, 128.2, 128.0, 127.2, 126.7, 60.1. HRMS (EI) Calcd for $C_{21}H_{18}O_2NSCl$ 383.0747, Found 383.0744. FT-IR(KBr, cm^{-1}): 3264 m, 3061 m, 3034 m, 2936 m, 2819 m, 1649 m, 1585 s, 1574 s, 1497 s, 1475 s, 1456 s, 1416 s, 1695 s, 1332 s, 1275 s, 1177 s, 1155 s, 1089 s, 1017 s.

N-[(2*E*)-1,3-diphenyl-2-propen-1-yl]-4-(trifluoromethyl)-benzenesulfonamide (3ae)

R_f = 0.54 (40% ethyl acetate/hexane). White solid. Mp: 109-110 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): 7.78-7.72 (*m*, 2 H), 7.30-7.09 (*m*, 12 H), 6.42 (*d*, *J* = 16.0 Hz, 1 H), 6.12 (*dd*, 15.6, 6.40 Hz, 1 H), 5.36-5.33 (*m*, 1 H), 5.20 (*t*, *J* = 6.40 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 100 MHz): 151.9, 139.4, 139.1, 135.9, 132.7, 129.5, 128.9, 128.7, 128.3, 128.2, 128.0, 127.2, 126.6, 121.6, 120.8, 60.2. HRMS (EI) Calcd for $C_{22}H_{18}O_3NSF_3$ 433.0959, Found 433.0966. FT-IR(KBr, cm^{-1}): 3263 m, 3029 m, 1650 m, 1599 s, 15879 s, 1497 s, 1457 s, 1431 s, 1327 s, 1255 s, 1213 s, 1164 s, 1095 s, 1041 s.

N-[(2*E*)-1,3-diphenyl-2-propen-1-yl]-4-nitrobenzenesulfonamide (3af) [30]

R_f = 0.50 (40% ethyl acetate/hexane). White solid. ^{1}H NMR ($CDCl_3$, 400 MHz): 8.14-8.10 (*m*, 2 H), 7.87-7.84 (*m*, 2 H), 7.30 -

7.15 (*m*, 10 H), 6.42 (*d*, *J* = 16.0 Hz, 1 H), 6.09 (*dd*, *J* = 16.0, 7.00 Hz, 1 H), 5.25 (*t*, *J* = 7.00 Hz, 1 H), 5.07 (*d*, *J* = 7.60 Hz). ^{1}H NMR (DMSO-d_6, 400 MHz): 8.83 (*d*, *J* = 8.80 Hz, 1 H), 8.18 (*d*, *J* = 8.60 Hz, 2 H), 7.92 (*d*, *J* = 8.60 Hz, 2 H), 7.26-7.16 (*m*, 10 H), 6.28 (*d*, *J* = 16.0 Hz, 1 H), 6.09 (*dd*, *J* = 16.0, 8.00 Hz, 1 H), 5.09 (*t*, *J* = 8.00 Hz, 1 H). ^{13}C NMR (DMSO-d_6, 100 MHz): 149.0, 147.1, 140.1, 135.7, 130.7, 128.5, 128.4, 128.2, 127.8, 127.4, 127.0, 126.2, 124.1, 59.5. HRMS (EI) Calcd for $C_{21}H_{18}O_4N_2S$ 394.0987, Found 349.1007. FT-IR(KBr, cm^{-1}): 3287 s, 1606 w, 1529 s, 1499 m, 1457 m, 1420 m, 1345 s, 1336 s, 1314 m, 1158 s, 1088 m, 1031 m.

_N_-[(2_E_)-1,3-diphenyl-2-propen-1-yl]-methanesulfonamide (3ag) [8c]

R_f = 0.36 (40% ethyl acetate/hexane). White solid. ^{1}H NMR ($CDCl_3$, 400 MHz): 7.41-7.26 (*m*, 10 H), 6.63 (*d*, *J* = 16.0 Hz, 1 H), 6.34 (*dd*, *J* = 16.0, 6.80 Hz, 1 H), 5.30 (*t*, *J* = 6.60 Hz, 1 H), 4.80 (*brs*, 1 H), 2.79 (*s*, 3 H). ^{13}C NMR ($CDCl_3$, 100 MHz): 140.0, 136.0, 132.7, 129.2, 128.8, 128.53, 128.46, 128.4, 127.3, 126.8, 59.9, 42.4. HRMS (EI) Calcd for $C_{16}H_{17}O_2NS$ 287.0980, Found 287.0994. FT-IR(KBr, cm^{-1}): 3306 m, 1651 m, 1497 m, 1458 m, 1432 s, 1417 s, 1353 s, 1315 s, 1265 s, 1154 s, 1086 m, 1040 s.

_N_-[(2_E_)-1,3-diphenyl-2-propen-1-yl]- 2-thiophenesulfonamide (3ah) [31]

R_f = 0.47 (40% ethyl acetate/hexane). White solid. ^{1}H NMR ($CDCl_3$, 400 MHz): 7.49-7.44 (*m*, 2 H), 7.29-7.23 (*m*, 10 H), 6.95-6.93 (*m*, 1 H), 6.45 (*d*, *J* = 16.0 Hz, 1 H), 6.18 (*dd*, *J* = 16.0, 6.40 Hz, 1 H), 5.21 (*t*, *J* = 7.20 Hz, 1 H), 5.18-5.05 (*brs*, 1 H). ^{13}C NMR ($CDCl_3$, 100 MHz): 141.9, 139.5, 136.1, 132.8, 132.4, 132.1, 129.0, 128.7, 128.2, 128.1, 127.3, 127.2, 126.7, 30.1. HRMS (EI) Calcd for $C_{19}H_{17}O_2NS_2$ 355.0701, Found 355.0746. FT-IR(KBr, cm^{-1}): 3265 s, 3095 m, 1494 m, 1456 m, 1437 s, 1403 m, 1343 s, 1326 s, 1232 m, 1155 s, 1091 s, 1067 m, 1020 s.

_N_-[(2_E_)-1,3-diphenyl-2-propen-1-yl]-4-fluoro- benzamide (3aj)

R_f = 0.44 (40% ethyl acetate/hexane). White solid. Mp: 141-142 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): 7.86-7.81 (*m*, 2 H), 7.44-7.22 (*m*, 10 H), 7.14-7.09 (*m*, 2 H), 6.61 (*d*, *J* = 16.0 Hz, 1 H), 6.47-6.41 (*m*, 2 H), 6.00 (*t*, *J* = 7.20 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): 165.6, 164.9 (*d*, $J_{C\text{-}F}$ = 253.9 Hz), 140.8, 136.4, 132.0, 130.6 (*d*, $J_{C\text{-}F}$ = 2.9 Hz), 129.6 (*d*, $J_{C\text{-}F}$ =10.4 Hz), 129.1, 128.7, 128.0 (*d*, $J_{C\text{-}F}$ = 2.9 Hz), 127.4, 126.7, 115.8 (*d*, $J_{C\text{-}F}$ = 22.1 Hz), 55.5. HRMS (EI) Calcd for $C_{22}H_{18}ONF$ 331.1372, Found 331.1365. FT-IR(KBr, cm^{-1}): 3341 s, 3029 m, 1635 s, 1603 s, 1593 m, 1541 s, 1499 s, 1449 s, 1351 m, 1341 m, 1314 m, 1286 m, 1268 m, 1238 s, 1158 m, 1097 m.

N-[(2E)-1,3-diphenyl-2-propen-1-yl]-4-methoxy-benzamide (3ak) [19a]

R_f = 0.39 (40% ethyl acetate/hexane). White solid. Mp: 75-76 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): 7.71 (*d*, *J* = 8.80 Hz, 2 H), 7.29-7.17 (*m*, 10 H), 6.78 (*d*, *J* = 8.80 Hz, 2 H), 6.36 (*d*, *J* = 16.0 Hz, 1 H), 6.10 (*dd*, *J* = 16.0, 6.80 Hz, 1 H), 5.51-5.49 (*m*, 1H), 5.11 (*t*, *J* = 7.00 Hz, 1 H), 3.73 (*s*, 3 H). ^{13}C NMR ($CDCl_3$, 100 MHz): 162.8, 139.8, 136.2, 132.4, 132.2, 129.6, 128.9, 128.6, 128.4, 128.0, 127.2, 126.7, 114.1, 59.9, 55.6. HRMS (EI) Calcd for $C_{23}H_{21}O_2N$ 343.1572, Found 343.1566. FT-IR(KBr, cm^{-1}): 3348 m, 1625 s, 1607 s, 1574 m, 1538 s, 1504 s, 1448 m, 1348 m, 1322 m, 1302 m, 1302s, 1254 s, 1177 s, 1107 w, 1028 m.

_N_-[(2_E_)-1,3-diphenyl-2-propen-1-yl]-benzamide (3al) [6a]

R_f 0.43 (40% ethyl acetate/hexane). White solid. ^{1}H NMR ($CDCl_3$, 400 MHz): 7.83 (*d*, *J* = 7.60 Hz, 2 H), 7.53-7.49 (*m*, 1 H), 7.45-7.22 (*m*, 12 H), 6.64-6.60 (*m*, 2 H), 6.45 (*dd*, *J* = 16.0, 6.00 Hz, 1 H), 6.03 (*t*, *J* = 7.00 Hz 1 H). ^{13}C NMR ($CDCl_3$, 100 MHz): 166.6, 140.9, 136.5, 134.4, 131.9, 131.8, 129.0, 128.9, 128.74, 128.69, 128.0, 127.96, 127.92, 127.4, 127.2, 126.7, 55.3. HRMS (EI) Calcd for $C_{22}H_{19}ON$ 313.1467, Found 313.1460. FT-IR(KBr, cm^{-1}): 3352 s, 1635 s, 1602 m, 1578 m, 1516 s, 1487 s, 1456 m, 1363 m, 1312 m, 1249 w, 1204 m, 1079 w, 1071 m, 1043 w, 1026 m.

_N_-[(2_E_)-1,3-diphenyl-2-propen-1-yl]-propanamide (3am)

*R*f = 0.24 (40% ethyl acetate/hexane). White solid. Mp: 117-118 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): 7.38-7.21 (*m*, 10 H), 6.51 (*d*, *J* = 16.0 Hz, 1 H), 6.33 (*dd*, *J* = 16.0, 6.40 Hz, 1 H), 6.22 (*d*, *J* = 8.40 Hz, 1 H) 5.82 (*t*, *J* = 7.20 Hz, 2 H), 2.26 (*dq*, *J* = 8.00, 1.60 Hz, 2 H), 1.17 (*t*, *J* = 8.00 Hz, 3 H). ^{13}C NMR ($CDCl_3$, 100 MHz) :173.0, 141.1, 136.5, 131.3, 129.1, 128.8, 128.6, 127.8, 127.7, 127.2, 126.6, 54.7, 29.8, 9.9. HRMS (EI) Calcd for $C_{18}H_{19}ON$ 265.1467, Found 265.1455. FT-IR(KBr, cm^{-1}): 3314 s, 3030 m, 2978 m, 2938 w, 1646 s, 1527 s, 1495 m, 1372 m, 1275 m, 1231 m.

_N_-(4-nitrophenyl)-_α_-[(1_E_)-2-phenylethenyl]-benzenemethanamine (3an) [6a]

R_f = 0.56 (40% ethyl acetate/hexane). Yellow viscose oil. ^{1}H NMR ($CDCl_3$, 400 MHz): 8.08-8.04 (*m*, 2 H), 7.41-7.24 (*m*, 10 H), 6.63-6.55 (*m*, 3 H), 6.38 (*dd*, *J* = 16.2, 5.80 Hz, 1 H), 5.23-5.19 (*m*, 1 H), 4.91-4.89 (*m*, 1 H). ^{13}C NMR ($CDCl_3$, 100 MHz): 152.2, 140.4, 138.7, 136.1, 132.4, 129.3, 128.8, 128.7, 128.35, 128.30, 127.3, 126.7, 126.4, 112.3, 60.2. HRMS (EI) Calcd for $C_{21}H_{18}O_2N_2$ 330.1368, Found 330.1359. FT-IR(KBr, cm^{-1}): 3377 m, 1596 s, 1531 s, 1494 s, 1467 s, 1357 m, 1329 s, 1298 s, 1182 m, 1110 s, 1087 m.

_N_-(2-nitrophenyl)-_α_-[(1_E_)-2-phenylethenyl]-benzenemethanamine (3ao) [6a]

R_f = 0.58 (40% ethyl acetate/hexane). Yellow viscose oil. ^{1}H NMR ($CDCl_3$, 400 MHz): 8.55-8.53 (*m*, 1 H), 8.21 (*dd*, *J* = 8.80, 1.60 Hz, 1 H), 7.49-7.23 (*m*, 12 H), 6.85 (*d*, *J* = 8.40 Hz, 1 H), 6.69-6.61 (*m*, 2 H), 6.44 (*dd*, *J* = 16.0, 5.60 Hz, 2 H), 5.34 (*t*, *J* =

5.80 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 100 MHz): 144.3, 140.5, 136.18, 136.15, 132.5, 132.0, 129.2, 129.0, 128.7, 128.14, 128.10, 127.0, 126.8, 126.7, 116.0, 115.2, 59.8. HRMS (EI) Calcd for $C_{21}H_{18}O_2N_2$ 330.1368, Found 330.1364. FT-IR(KBr, cm^{-1}): 3377 m, 1618 s, 1572 s, 1512 s, 1450 m, 1416 m, 1347 s, 1257 s, 1152 m.

_N_-(4-bromophenyl)-_α_-[(1_E_)-2-phenylethenyl]-benzene-methanamine (3ap)

_R_f = 0.60 (40% ethyl acetate/hexane). Yellow viscose oil. ^{1}H NMR ($CDCl_3$, 400 MHz): 7.50-7.28 (*m*, 12 H), 6.68 (*d*, *J* = 16.0 Hz, 1 H), 6.59-6.55 (*m*, 2 H), 6.44 (*dd*, *J* = 16.0, 6.40 Hz, 1 H), 5.11 (*d*, *J* = 6.00 Hz, 1 H), 4.22 (*brs*, 1 H). ^{13}C NMR ($CDCl_3$, 100 MHz): 146.2, 141.6, 136.5, 131.9, 131.4, 130.2, 129.0, 128.8, 128.7, 127.9, 127.8, 127.2, 126.6, 126.5, 115.3, 109.4, 60.6. HRMS (EI) Calcd for $C_{21}H_{18}NBr$ 363.0623, Found 363.0617. FT-IR(KBr, cm^{-1}): 3410 m, 1690 w, 1595 s, 1495 s, 1450 s, 1394 m, 1315 s, 1294 s, 1259 m, 1241 m, 1178 m, 1121 w, 1073 s, 1027 w.

N-(4-chlorophenyl)-α-[(1E)-2-phenylethenyl]-benzene-methanamine (3aq) [8a]

R_f = 0.58 (40% ethyl acetate/hexane). Yellow viscose oil. ^{1}H NMR ($CDCl_3$, 400 MHz): 7.48-7.28 (*m*, 10 H), 7.19-7.12 (*m*, 2 H), 6.71-6.58 (*m*, 3 H), 6.47-6.39 (*m*, 1 H), 5.15-5.08 (*m*, 1 H), 4.19 (*brs*, 1 H). ^{13}C NMR ($CDCl_3$, 100 MHz): 145.8, 141.7, 136.6, 131.4, 130.3, 129.1, 129.0, 128.7, 127.9, 127.8, 127.3, 126.6, 122.4, 114.8, 60.8. HRMS (EI) Calcd for $C_{21}H_{18}NCl$ 319.1128, Found 319.1108. FT-IR(KBr, cm^{-1}): 3411 m, 1689 w, 1596 s, 1497 s, 1449 s, 1397 m, 1309 s, 1257 m, 1236 w, 1177 m, 1091 m.

_N_-(4-methoxyphenyl)-_α_-[(1_E_)-2-phenylethenyl]-benzene-methanamine (3ar) [32]

R_f = 0.61 (40% ethyl acetate/hexane). White solid. Mp: 75-76 ºC. ^{1}H NMR ($CDCl_3$, 400 MHz): 7.48-7.45 (*m*, 2 H), 7.41-7.36 (*m*, 4 H), 7.34-7.21 (*m*, 4 H), 6.78-6.75 (*m*, 2 H), 6.66-6.62 (*m*, 3 H), 6.42 (*dd*, *J* = 16.0, 5.60 Hz, 1 H), 5.04 (*d*, *J* = 6.40 Hz, 1 H), 3.74 (*s*, 3 H). ^{13}C NMR ($CDCl_3$, 100 MHz): 152.4, 142.5, 141.6, 136.8, 131.3, 131.0, 128.9, 128.7, 127.8, 127.6, 127.3, 126.6, 115.1, 114.9, 61.7, 55.9. HRMS (EI) Calcd for $C_{22}H_{21}ON$ 315.1623, Found 315.1652. FT-IR(KBr, cm^{-1}): 3393 m, 1597 m, 1587 m, 1508 s, 1467 s, 1446 s, 1400 s, 1336 s, 1313 s, 1277 m, 1250 s, 1234 s, 1181 s, 1170 s, 1119 m, 1088 m, 1062 m, 1032 s.

_N_-(4-methylphenyl)-_α_-[(1_E_)-2-phenylethenyl]-benzene-methanamine (3as)

R_f = 0.64 (40% ethyl acetate/hexane). Colorless viscose oil. ^{1}H NMR ($CDCl_3$, 400 MHz): 7.46-7.22 (*m*, 12 H), 6.97 (*d*, *J* = 7.60 Hz, 2 H), 6.66-6.57 (*m*, 3 H), 6.31 (*dd*, *J* = 16.0, 5.60 Hz, 1 H), 7.07 (*d*, *J* = 6.40 Hz, 1 H), 4.01 (*brs*, 1 H), 2.24 (*s*, 3 H). ^{13}C NMR ($CDCl_3$, 100 MHz): 145.1, 142.4, 136.9, 131.12, 131.08, 129.8, 128.9, 128.7, 127.8, 127.6, 127.4, 127.0, 126.7, 113.9, 61.1, 20.5. HRMS (EI) Calcd for $C_{22}H_{21}N$ 299.1674, Found 229.1682. FT-IR(KBr, cm^{-1}): 3407 m, 1616 m, 1518 s, 1465 m, 1449 m, 1412 w, 1317 m, 1301 m, 1259 m, 1237 w.

4-[[(2_E_)-1,3-diphenyl-2-propen-1-yl]amino]-benzonitrile (3at) [31]

R_f = 0.56 (40% ethyl acetate/hexane). White solid. ^{1}H NMR ($CDCl_3$, 400 MHz): 7.42-7.24 (*m*, 12 H), 6.64-6.59 (*m*, 3 H), 6.39 (*dd*, *J* = 16.0, 6.40 Hz, 1 H), 5.16 (*t*, *J* = 5.40 Hz, 1 H), 4.76 (*brs*, 1 H). ^{13}C NMR ($CDCl_3$, 100 MHz): 150.3, 140.7, 136.2, 133.7, 132.0, 129.1, 128.7, 128.1, 127.2, 126.6, 120.4, 113.2, 99.3, 60.0. HRMS (EI) Calcd for $C_{22}H_{18}N_2$ 310.1470, Found 310.1486. FT-IR(KBr, cm^{-1}): 3393 s, 2211 s, 1607 s, 1520 s, 1493 m, 1452 m, 1336 s, 1310 m, 1258 m, 1245 m, 1173 s, 1132 m, 1094 w.

_N_-[(2_E_)-1,3-bis(4-fluorophenyl)-2-propen-1-yl]-4-methyl-benzenesulfonamide (3ba)

R_f = 0.40 (40% ethyl acetate/hexane). White solid. Mp: 136-137 ºC. ^{1}H NMR ($CDCl_3$, 400 MHz): 7.63 (*d*, *J* = 8.40 Hz, 2H), 7.17-7.13 (*m*, 6 H), 6.98-6.90 (*m*, 4 H), 6.30 (*d*, *J* = 16.0 Hz, 2 H), 5.97 (*dd*, *J* = 16.0, 6.40 Hz, 1 H), 5.23 (*d*, *J* = 8.40 Hz, 1 H), 5.08 (*t*, *J* = 7.00 Hz, 1 H), 2.33 (*s*, 3 H). ^{13}C NMR ($CDCl_3$, 100 MHz): 162.6 (*d*, $J_{C\text{-}F}$ = 249.1 Hz), 162.4 (*d*, $J_{C\text{-}F}$ = 248.2 Hz), 143.6, 137.7, 135.5 (*d*, $J_{C\text{-}F}$ = 3.90 Hz), 132.2 (*d*, $J_{C\text{-}F}$ = 2.80 Hz), 131.3, 129.6, 128.9 (*d*, $J_{C\text{-}F}$ = 8.60 Hz), 128.2 (*d*, $J_{C\text{-}F}$ = 8.70 Hz), 127.8, 127.4, 115.7 (*d*, $J_{C\text{-}F}$ = 12.5 Hz), 115.5 (*d*, $J_{C\text{-}F}$ = 12.5 Hz), 59.2, 21.5. HRMS (EI) Calcd for $C_{22}H_{19}O_2NSF_2$ 399.1105, Found 399.1104. FT-IR(KBr, cm^{-1}): 3226 s, 1601 m, 1508 s, 1434 m 1324 s, 1306 m, 1222 s, 1162 s, 1151 s, 1095 m, 1037 s.

_N_-[(2_E_)-1,3-bis(4-methylphenyl)-2-propen-1-yl]-4-methyl-benzenesulfonamide (3ca)

R_f = 0.43 (40% ethyl acetate/hexane). White solid. Mp: 123-124 ºC. ^{1}H NMR ($CDCl_3$, 400 MHz): 7.65 (*d*, *J* = 8.00 Hz, 2 H), 7.17-7.07 (*m*, 10 H), 6.31 (*d*, *J* = 16.0 Hz, 1 H), 6.10 (*dd*, *J* = 16.0, 6.40 Hz, 1 H), 5.06 (*t*, *J* = 6.80 Hz, 1 H), 4.89-4.85 (*m*, 1 H), 2.34 (*s*, 1 H), 2.32 (*s*, 1 H), 2.30 (*s*, 1 H). ^{13}C NMR ($CDCl_3$, 100 MHz): 143.3, 137.94, 137.86, 137.77, 136.96, 133.5, 132.0, 129.55, 129.49, 129.3, 127.49, 127.46, 127.1, 126.6, 59.7, 21.6, 21.3, 21.2. HRMS (EI) Calcd for $C_{24}H_{19}O_2NS$ 391.1606, Found 391.1608. FT-IR(KBr, cm^{-1}): 3251 s, 1510 m, 1432 m, 1330 s, 1177 m, 1159 s, 1093 m, 1051 w.

4-Methyl-_N_-[(2_E_)-1-methyl-3-phenyl-2-propen-1-yl]-benzene-sulfonamide (3ea) [33]

R_f = 0.53 (40% ethyl acetate/hexane). White solid. ^{1}H NMR ($CDCl_3$, 400 MHz): 7.41-7.23 (*m*, 9 H), 6.62 (*d*, *J* = 16.0 Hz, 1 H), 6.34 (*dd*, *J* = 16.0, 6.40 Hz, 1 H), 5.29-5.24 (*m*, 2 H), 2.77 (*s*, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz):143.3, 138.1, 136.4, 130.5, 130.2, 129.75, 129.65, 129.5, 128.5, 127.7, 127.3, 126.5, 51.8, 22.0, 21.5. HRMS (EI) Calcd for $C_{17}H_{19}O_2NS$ 301.1136, Found

301.1142. FT-IR(KBr, cm^{-1}): 3234 s, 1597 s, 1494 s, 1451 s, 1434 s, 1376 m, 1325 s, 1160 s, 1139 m, 1088 s, 1067 s, 1021 m.

4-Methyl-*N*-[(2*E*)-1-phenyl-2-buten-1-yl]-benzenesulfonamide (3fa) [34]

R_f = 0.51 (40% ethyl acetate/hexane). White solid. Mp: 81-82 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): 7.76 (*d*, *J* = 8.40 Hz, 2 H), 7.29-7.21 (*m*, 5 H), 7.17-7.16 (*m*, 2 H), 6.30 (*d*, *J* = 16.0 Hz, 1 H), 5.84 (*dd, J* = 16.0, 7.00 Hz, 1 H), 4.76 (*d*, *J* = 7.20 Hz, 1 H), 4.12-4.06 (*m*, 1 H), 2.34 (*s*, 3 H), 1.28 (*d*, *J* = 6.80 Hz, 3 H). ^{13}C NMR ($CDCl_3$, 100 MHz): 143.4, 138.2, 136.3, 130.6, 130.2, 129.7, 128.6, 127.8, 127.4, 126.5, 51.8, 22.1, 21.6. HRMS (EI) Calcd for $C_{17}H_{19}O_2NS$ 301.1136, Found 301.1113. FT-IR(KBr, cm^{-1}): 3292 s, 1599 m, 1493 m, 1447 s, 1429 s, 1377 m, 1340 s, 1317 s, 1303 s, 1156 s, 1147 s, 1120 m, 1092 s, 1072 m, 1047 m.

***N*-2-cyclohexen-1-yl-4-methyl-benzenesulfonamide (3ga) [35]**

R_f = 0.43 (40% ethyl acetate/hexane). White solid. ^{1}H NMR ($CDCl_3$, 400 MHz): 7.75 (*d*, *J* = 8.40 Hz, 2 H), 7.23 (*d*, *J* = 8.40 Hz, 2 H), 5.68-5.64 (*m*, 1 H), 5.35-5.28 (*m*, 2 H), 3.72 (*brs*, 1 H), 2.35 (*s*, 3 H), 1.95-1.75 (*m*, 2 H), 1.65-1.41 (*m*, 4 H). ^{13}C NMR ($CDCl_3$, 100 MHz): 143.0, 138.3, 131.1, 129.5, 127.0, 126.9, 48.8, 30.0, 24.3, 21.4, 19.3. HRMS (EI) Calcd for $C_{13}H_{17}O_2NS$ 251.0980, Found 251.0982. FT-IR(KBr, cm^{-1}): 3274 s, 1916 m, 1650 m, 1597 m, 1494 m, 1446 s, 1421 s, 1389 m, 1352 m, 1321 s, 1286 m, 1160 s, 1090 s, 1068 s.

***N*-(diphenylmethyl)-4-methyl-benzenesulfonamide (3ha) [36]**

R_f = 0.44 (40% ethyl acetate/hexane). White solid. ^{1}H NMR ($CDCl_3$, 400 MHz): 7.56 (*d*, *J* = 8.00 Hz, 2H), 7.23-7.17 (*m*, 6 H), 7.13-7.10 (*m*, 6 H), 5.80 (*d*, *J* = 7.60 Hz, 1 H), 5.45-5.40 (*m*, 1 H), 2.37 (*s*, 3 H). ^{13}C NMR ($CDCl_3$, 100 MHz): 143.3, 140.7, 137.5, 129.4, 128.6, 127.6, 127.5, 127.3, 61.4, 21.6. HRMS (EI) Calcd for $C_{20}H_{19}O_2NS$ 337.1136, Found 337.1117. FT-IR(KBr, cm^{-1}): 3249 s, 1599 m, 1495 m, 1451 s, 1316 s, 1161 s, 1096 m, 1086 m, 1058 m, 1028m

.

Acknowledgements

This study was partly supported by JST CREST Grant Number JPMJCR17P1, Japan and JSPS KAKENHI Grant Number 19K05156, Japan. We also thank associate professor Eiko Yasui for assistance with HRMS.

Keywords: Allyl alcohols • Amidation • Solid acid catalyst • H-*BEA Zeolite

[1] For examples a) M. Johannsen, K. A. Jørgensen, *Chem. Rev*., **1998**, *98*, 1689-1708; b) R. Cheikh, R. Chaabouni, A. Laurent, P. Mison, A. Nafti, *Synthesis*, **1983**, 685-700; c) Z.-Y. Wei, E. E. Knaus, *Synthesis*. **1994**, 1463-1466; d) A. Spaltenstein, P. A. Carpino, F. Miyake, P. B. Hopkins, *J. Org. Chem*. **1987**, *52*, 3759-3766; e) E. M. Skoda, G. C. Davis, P. Wipf, *Organic Process Research and Development*, **2012**, *16*, 26-34; f) K. Takao, K. Toda, T. Saito, Y. Sugita, *Chem. Pharm. Bull*., **2017**, *65*, 1020-1027; g) J. Liu, L. Wang, X. Zheng, A. Wang, M. Zhu, J. Yu, Q. Shen, *Tetrahedron Letters*, **2012**, *53*, 1843-1846; h) C. Chazalette, M. Riviere-Baudet, C. T. Supuran, A. Scozzafava, *J. Enzyme. Inhibition*, **2001**, *16*, 475-489; i) F. Inagaki, S. Hira, C. Mukai, *Synlett*, **2017**, *28*, 2143-2146; j) P. Prediger, L. F. Barbosa, Y. Génisson, C. R. D. Correia, *J. Org. Chem*., **2011**, *76*, 7737-7749; k) M. A. Davis, D. A. Barnette, N. R. Flynn, A. S. Pidugu, S. J. Swamidass, G. Boysen, G. P. Miller, *Chem. Rec. Toxicol*., **2019**, *32*, 1151-1164; l) E. M. Skoda, G. C. Davis, P. Wipf, *Org. Process Res. Dev*., **2012**, *16*, 26-34; m) W. K. Amery, *Headache*., **1983**, *23*, 70-74; n) K. D. Shanti, M. D. Shanti, J. S. Meshram, *J. Comput. Methods Mol. Des.,* **2016**, *6*, 13-19.

[2] For examples a) B. G. Das, R. Nallagonda, P. J. Ghorai, *Org. Chem.*, **2012**, *77*, 5577-5583; b) T. Ohshima, K. Mashima, *J. Synth. Org. Chem.*, **2012**, *70*, 1145-1156; c) K. Utsunomiya, Y. Miyamoto, J. Ipposhi, T. Ohshima, K. Mashima, *Org. Lett*., **2007**, *9*, 3371-3374; d) J. Jing, X. Huo, J. Shen, Q. Meng, W. Zhang, *Chem. Commun*., **2017**, *53*, 5151-5154; e) R. Ghosh, A. Sarkar, *J. Org. Chem.*, **2011**, *76*, 8508-8512; f) J. Xie, C. Qiao, M. M. Belmonte, E. C. Escudero-Adán, A. W. Kleij, *ChemSusChem*, **2019**, *12*, 3152-3158; g) Z. Wu, K. L. Hull, *Chem. Sci*., **2016**, *7*, 969-975; h) T. T. Nguyen, K. L. Hull, *ACS Catal.*, **2016**, *6*, 8214-8218; i) S. W. Krabbe, V. S. Chan, T. S. Franczyk, S. Shekhar, J. G. Napolitano, C. A. Presto, J. A. Simanis, *J. Org. Chem*, **2016**, *81*, 10688-10697; j) U. Jana, S. Maiti, S. Biswas, *Tetrahedron Letters*, **2008**, *49,* 858-862; k) M. Subaramanian, S. P. Midya, P. M. Ramar, E. Balaraman, *Org. Lett.*, **2019**, *21*, 8899-8903; l) V. G. Landge, A. Mondal, V. Kumar, A. Nandakumar, E. Balaraman, *Org. Biomol. Chem*., **2018**, *16*, 8175-8180; m) S. P. Midya, J. Pitchaimani, V. G. Landge, V. Madhu, E. Balaraman, *Catal. Sci. Technol*., **2018**, *8*, 3469-3473; n) S. P. Midya, A. Mondal, A. Begum, *Synthesis*. **2017**, *49*, 3957-3961; o) S. P. Midya, J. Rana, J. Pitchaimani, A. Nandakumar, V. Madhu, E. Balaraman, *ChemSusChem*, **2018**, *11*, 3911-3916.

[3] T. Hayashi, A. Yamamoto, Y. Ito, E. Nishioka, H. Miura, K. Yanagi, *J. Am. Chem. Soc.*, **1989**, *111*, 6301-6311.

[4] A. Lei, X. Lu, *Org. Lett.*, **2000**, *2*, 2357-2360.

[5] B. G. Das, R. Nallagonda, P. Ghorai, *J. Org. Chem.*, **2012**, *77*, 5577-5583.

[6] a) H. Yang, L. Fang, M. Zhang, C. Zhu, *Eur. J. Org. Chem.*, **2009**, *5*, 666-672; b) V. Bagchi, P. Paraskevopoulou, P. Das, L. Chi, Q. Wang, A. Choudhury, P. Stavropoulos, *J. Am. Chem. Soc.*, **2014**, *136*, 11362-11381.

[7] H. Qin, N. Yamagiwa, S. Matsunaga, M. Shibasaki. *Angew. Chem. Int. Ed.*, **2006**, *46*, 409-413.

[8] a) M. Georgy, V. Boucard, O. Debleds, C. D. Zotto, J. M. Campagne, *Tetrahedron*, **2009**, *65*, 1758-1766; b) S. Guo, F. Song, Y. Liu, *Synlett*, **2007**, 964-968; c) X. Giner, P. Trillo, C. Nájera, *J. Organomet. Chem.*, **2010**, *696*, 357-361.

[9] W. Huang, Q. S. Shen, J. L. Wang, X. G. Zhou, *Chinese J. Chem.*, **2008**, *26*, 729-735.

[10] a) H. X. Zheng, Z. F. Xiao, C. Z. Yao, Q. Q. Li,X. S., Ning,Y. B. Kang, Y. Tang, *Org. Lett*., **2015**, *17*, 6102-6105; b) P. Trillo, A. Baeza, C. Nájera, *ChemCatChem*, **2013**, *5*, 1538-1542.

[11] a) A. Cullen, A. J. Muller, D. B. G. Williams, *RSC Advance*s, **2017**, *7*, 42168-42171; b) T. Ohshima, J. Ipposhi, Y. Nakahara, R. Shibuya, K. Mashima, *Adv. Synth. Catal*., **2012**, *354*, 2447-2452.

[12] a) A. Zhu, L. Li, J. Wang, K. Zhuo, *Green Chemistry*, **2011**, *13*, 1244-1250; b) G. P. Fan, Z. Liu, G. W. Wang, *Green Chemistry*, **2013**, *15*, 1659-1664.

[13] T. Sakuramoto, T. Hirao, M. Tobisu, T. Moriuchi, *ChemCatChem*, **2019**, *11*, 1175-1178.

[14] a) S. Shirakawa, S. Shimizu, *Synlett*, **2008**, 1539-1542; b) P. Trillo, A. Baeza, N. Carmen, *Eur. J. Org. Chem.*, **2012**, 2929-2934; c) F. Han, L. Yang, Z. Li, C. Xia, *Adv. Synth. Catal*., **2012**, *354*, 1052-1060.

[15] M. Gómez-Martínez, A. Baeza, D. A. Alonso, *ChemCatChem*, **2017**, *9*, 1032-1039.

[16] G. W. Wang, Y. B. Shen, X. L. Wu, *Eur. J. Org. Chem.*, **2008**, 4367-4371.

[17] a) W. Wu, W. Rao, Y. Q. Er, J. K. Loh, C. Y. Poh, P. W. H. Chan, *Tetrahedron Letters*, **2008**, *49*, 2620-2624; b) Z. Liu, D. Wang, Y. Chen, *Lett. Org. Chem.*, **2011**, *8*, 73-80.

[18] M. Zhuang, H. Du, *Org. Biomol. Chem.*, **2014**, *12*, 4590-4593.

[19] a) H. Li, J. Dong, K. Tian, *Eur. J. Org. Chem.*, **2008**, *21*, 3623-3626; b) P. Trillo, A. Baeza, C. Nájera, *J. Org. Chem.*, **2012**, *77*, 7344-7354.

[20] a) X. Xu, H. Wu, Z. Li, X. Sun, Z. Wang, *Tetrahedron*, **2015**, *71*, 5254-5259; b) L. Li, A. Zhu, Y. Zhang, X. Fan, G. Zhang, *RSC Advances*, **2014**, *4*, 4286-4291; c) J. S. Yadav, V. B. Subba Reddy, T. Srinivasa Rao, B. Bala, M. Krishna, G. G. K. S. Narayana Kumar, *Chem. Lett*., **2007**, *36*, 1472-1473; d) A. Grau, A. Baeza, E. Serrano, J. García-Martínez, C. Nájera, *ChemCatChem*, **2015**, *7*, 87-93; e) H. Gu, X. Sun, Y. Wang, H. Wu, P. Wu, *RSC Advances*, **2018**, *8*, 1737-1743.

[21] *For examples* a) P. B. Venuto, *Microporous Materials*, **1994**, *2*, 297-411; b) A. Corma, H. García, *Catalyst Today*, **1997**, *38*, 257-308; c) X. Wang, J. Zeng, X, Lu, J. Xin, S. Zhang, *Ind. Eng. Chem. Res.*, **2019**, *58*, 11841-11848; d) M. Jeganathan, K. Pitchumani, *ACS Sustainable Chem. Eng.*, **2014**, *2*, 1169-1176; e) S. Inagaki, K. Sato, S. Hayashi, J. Tatami, T. Kubota, T. Wakahara, *ACS Appl. Mater. Interfaces*, **2015**, *7*, 4488-4502; f) M. Arshadi, M. Ghiaci, A. Gil, *Ind. Eng. Chem. Res.*, **2010**, *49*, 5504-5510; g) A. Corma, *Chem. Rev.*, **1995**, *95*, 559-614; h) A. Corma, *Chem. Rev*., **1997**, *97*, 2373-2420; i) A. Corma, H. García, F. X. L. I Xamena, *Chem. Rev.*, **2010**, *110*, 4606-4655; j) M. E. Davis, *Chem. Res.*, **1993**, *26*, 111-116; k) S. Chassaing, M. Kumarraja, P. Pale, J. Sommer, *Org. Lett.*, **2007**, *9*, 3889-3892; l) S. Chassaing, V. Beneteau, B. Louis, P. Pale, *Current Organic Chemistry*, **2017**, *21*, 779-793; m) B. Louis, M. Pereira, F. Santos, P. Esteves, J. Sommer, *Chem. Eur. J.*, **2010,** *16*, 573-576.

[22] *Example of similar reaction mechanism report.* P. Thiruphathi, S. S. Kim, *Tetrahedron*, **2010**, *66*, 2995-3003.

[23] C.-K. Chan, Y.-L. Tsai, M.-Y. Chang, *Tetrahedron*, **2017**, *73*, 3368-3376.

[24] R. Umeda, Y. Takahashi, T. Yamamoto, H. Iseki, I. Osaka, Y. Nishiyama, *J. Organomet. Chem.*, **2018**, *877*, 92-101.

[25] B.-Z. Ren, M. Ablise,X.-C. Yang, *Med. Chem. Res.*, **2017**, *26*, 1871-1883.

[26] M. A. Tandiary, Y. Masui, M. Onaka, *RSC Advances*, **2015**, *5*, 15736-15739.

[27] J. N. Moorthy, S. Samanta, A. L. Koner, W. M. Nau, *J. Am. Chem. Soc.*, **2008**, *130*, 41, 13608-13617.

[28] *Referenced spectrum:* P. Evans, P. Joohnson, R. J. K. Taylor, *Eur. J. O. C.*, **2006**, *7*, 1740-1754.

[29] H. Stamm, D. Speth, *Chemische Berichte*, **1989**, *122*, 1795-1797.

[30] Y. Nakao, M. Takeda, J. Chen, T. Hiyama, Y. Ichikawa, Y.; R. Shintani, T. Hayashi, *Chem. Lett.*, **2008**, *37*, 290-291.

[31] T. Ohshima, Y. Nakahara, J. Ipposhi, Y. Miyamoto, K. Mashima, *Chem. Commun*., **2011**, *47*, 8322-8324.

[32] C. Denhez, S. Médégan, F. Hélion, J.-L. Namy, J.-L. Vasse, J. Szymoniak, *Org. Lett.*, **2006**, *8*, 2945-2947.

[33] B. Sreedhar, V. Ravi, D. Yada, *Tetrahedron Lett.*, 2011, 52, 1208-1212

[34] E. E.. Lee, R. A. Batey, *J. Am. Chem. Soc*., **2005**, *127*, 14887-14893.

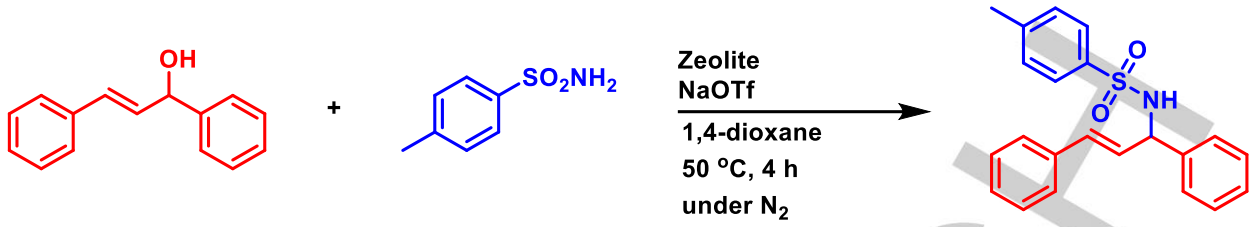
[35] X. Giner, C. Nájera, *Org. Lett.*, **2008**, *10*, 2919-2922.

[36] a) Z. S. Qureshi, K. M. Deshmukh, P. J. Tambade, K. P. Dhake B. M. Bhanage, *Eur. J. Org. Chem.*, **2010**, *32*, 6233-6238; b) A. Bakar, Md., Y. Suzuki, M. Sato, Masayuki, *Chem. Pharm. Bull.*, **2008**, *56*, 973-976.

10.1002/ejoc.202000296

Entry for the Table of Contents

Key topic: Allyl alcohols • Amidation • Solid acid catalyst • H-*BEA Zeolite



Towards efficient conversion of ally alcohol into value-added compounds: The first examples of zeolite catalyzed substitution of the hydroxy group in allyl alcohols with nucleophiles were developed. The zeolite catalyzed substitution reaction was broadly adaptable to substrates under relatively mild reaction conditions.