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TMSCl-Mediated Synthesis of α,β-Unsaturated Amides via C−C Bond Cleavage and C−N Bond Formation of Propargyl Alcohols with Trimethylsilyl Azide

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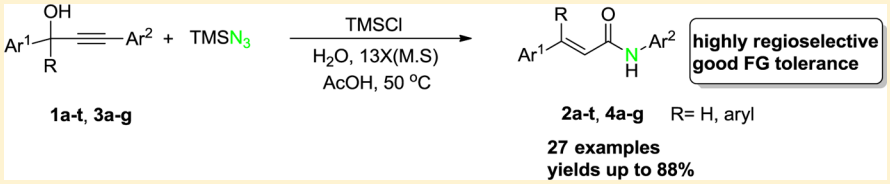
Supporting Information



ABSTRACT: A new method with high efficiency for the synthesis of α,β-unsaturated amides from the easily prepared propargyl alcohols and $TMSN_3$ using TMSCl as an acid promoter is developed. A wide variety of α,β-unsaturated amides were produced in moderate to excellent yields. Mechanistic studies indicate that this transformation involves TMSCl-mediated allenylazide intermediate formation, C−C bond cleavage, and C−N bond formation. Significantly, this reaction shows good functional group compatibility and high regioselectivity, with a relatively short reaction time and inexpensive reagents.

INTRODUCTION

In recent years, the transformations of vinyl azides have become powerful and novel methods for the constructions of various nitrogen-containing molecules and have attracted an increasing attention for their potential intrinsic reactivity.[1] Furthermore, the azide group close to the alkene unit plays an important role in improving the reactivity of alkenes,[2] which stimulates chemists to use vinyl azides as enamine-type nucleophiles to react with electrophiles for the efficient construction of bioactive compounds, especially amide derivatives. Amides are useful structural skeletons in a wide variety of pharmaceuticals, bioactive molecules, and functional materials.[3] Therefore, the development of atom- and step-economical approaches to the synthesis of the amide-containing compounds has attracted considerable attention in organic chemistry.[4,5] Recently, the Jiao group developed an interesting method for the synthesis of amides from alkynes.[6] It was based on a gold-catalyzed transformation of alkynes with $TMSN_3$, which involved a vinyl azide intermediate [Scheme 1, eq (1)]. More recently, Chiba and co-workers reported the remarkable conversion of vinyl azides into amides using carbon electrophiles (E^+) and $BF_3{\cdot}OEt_2$ as a Lewis acid promoter [Scheme 1, eq (2)].[7]

Inspired by these intriguing studies and based on our work on the application of propargylic alcohols in organic synthesis, we envisioned that it was possible for allenylazides instead of vinyl azides to react with electrophiles for their high nucleophilicities similar to alkene. Such transformations should be highly dependent on the synthesis of the allenylazides. However, the synthesis of allenylazides remained challenging due to their extreme instability.[8] Fortunately, chemists have developed another strategy as an alternative method in situ to form allenylazides by the nucleophilic addition of azides to propargyl alcohols. In 2013, Tanimoto and co-workers reported a Lewis acid mediated synthesis of trizoles from propargyl alcohols and organic azides via allenylazide intermediates [Scheme 1, eq (3)].[9] In 2014, the Jiao group reported the reaction of terminal alkynols with $TMSN_3$ in the presence of sulfuric acid to afford alkenyl nitriles via allenylazide intermediates [Scheme 1, eq (4)].[10] Despite the significant progress in the area of C−N bond formation through allenylazides, the synthesis of amides from easily prepared propargyl alcohols and $TMSN_3$ through C−C bond cleavage and C−N bond formation is still extremely attractive and challenging. More recently, our group reported Lewis acid mediated propargyl alcohols with $TMSN_3$ through allenylazide intermediates to produce tetrazoles [Scheme 1, eq (5)].[11]The proposed mechanism involves the Schimidt-type rearrangement of allenylazide intermediate to form intermediate **I**. Thus, we envisioned that, if the intermediate **I** could be trapped by water, the overall transformation would lead to the formation of the α,β-unsaturated amides. Herein, we report a new method for the synthesis of amides by a C−C bond cleavage and C−N bond formation strategy that features allenylazides as intermediates through nucleophilic addition of azides to propargyl alcohols.

RESULTS AND DISCUSSION

Our study to explore the designed reaction started with propargyl alcohol **1a** and $TMSN_3$ in the presence of acid as the

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Scheme 1. New Strategies for the Synthesis of Amides via C−C Bond Cleavage and C−N Bond Formation

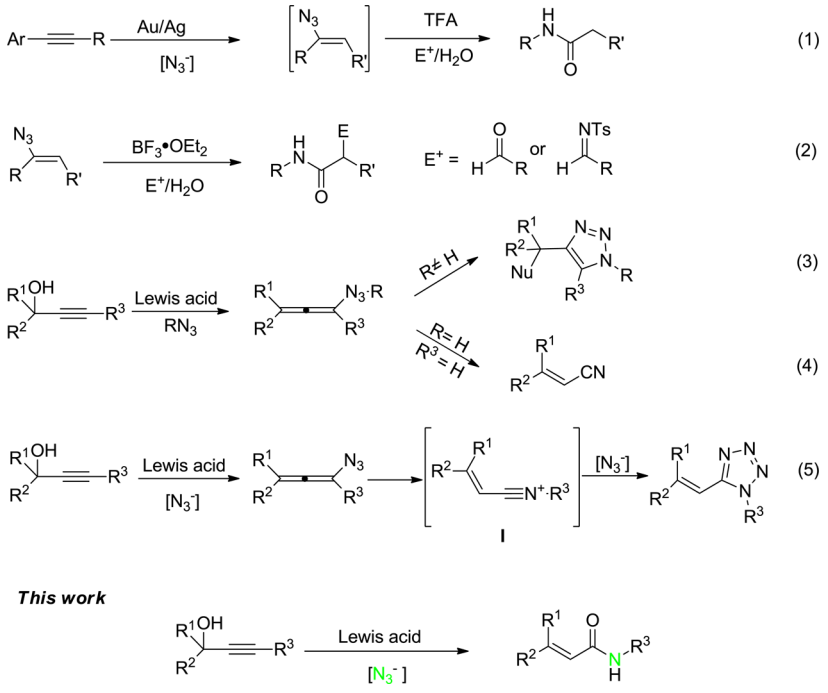
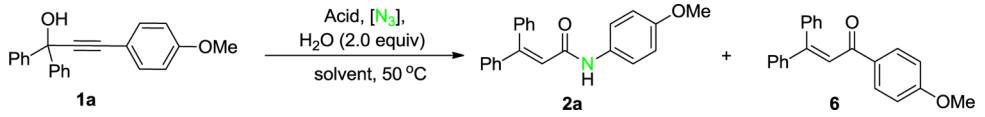


Table 1. Optimization of the Reaction Conditions[a]



				yield (%)	
entry	acid (equiv)	$TMSN_3$ (equiv)	solvent	**2a**	**6**
1	TMSCl (1.0)	2.0	MeCN	35	30
2	TMSCl (1.0)	2.0	CH_3NO_2	45	32
3	TMSCl (1.0)	2.0	HOAc	50	34
4	TMSCl (1.0)	2.0	toluene	trace[b]	0
5	TMSCl (1.0)	2.0	1,4-dioxane	trace[b]	0
6	TMSCl (1.0)	3.0	HOAc	65	23
7	TFA (1.0)	3.0	HOAc	40	35
8	BF_3·OEt_2 (1.0)	3.0	HOAc	<5	34
9	*p*-TsOH (1.0)	3.0	HOAc	25	29
10	TMSCl (2.0)	3.0	HOAc	70	18
11	TMSCl (2.0)	4.0	HOAc	75	15
12	TMSCl (3.0)	4.0	HOAc	82	8
13[c]	TMSCl (3.0)	4.0	HOAc	67	7
14[d]	TMSCl (3.0)	4.0	HOAc	70	22
15[e]	TMSCl (3.0)	4.0	HOAc	55	21
16[f]	TMSCl (3.0)	4.0	HOAc	57	30
17[g]	TMSCl (3.0)	4.0	HOAc	62	26
18[h]	TMSCl (3.0)	4.0	HOAc	75	16
19[i]	TMSCl (3.0)	4.0	HOAc	60	22
20[j]	TMSCl (3.0)	4.0	HOAc	35	17
21[k]	TMSCl (3.0)	4.0	HOAc	trace	76
22[l]	conc. HCl (3.0)	4.0	HOAc	64	25
23	AcCl (3.0)	4.0	HOAc	60	27

[a]Unless otherwise noted, all reactions were performed with 0.1 mmol of **1a**, and molecular sieves (13X; 30 mg.) in solvent (1.0 mL) at 50 °C for 2.0 h. [b]No product was detected by TLC. [c]1.0 equiv of H_2O. [d]3.0 equiv of H_2O. [e]In the absence of molecular sieves (13X). [f]4 Å molecular sieves were used instead of 13X molecular sieves. [g]5 Å molecular sieves were used instead of 13X molecular sieves. [h]At 70 °C. [i]At room temperature for 7.0 h. [j]NaN_3 was used instead of $TMSN_3$. [k]DPPA was used instead of $TMSN_3$. [l]In the absence of water. DPPA = diphenylphosphoryl azide. TMS = trimethylsilyl, TFA = trifluoroacetic acid, *p*-TsOH = *p*-toluenesulfonic acid.

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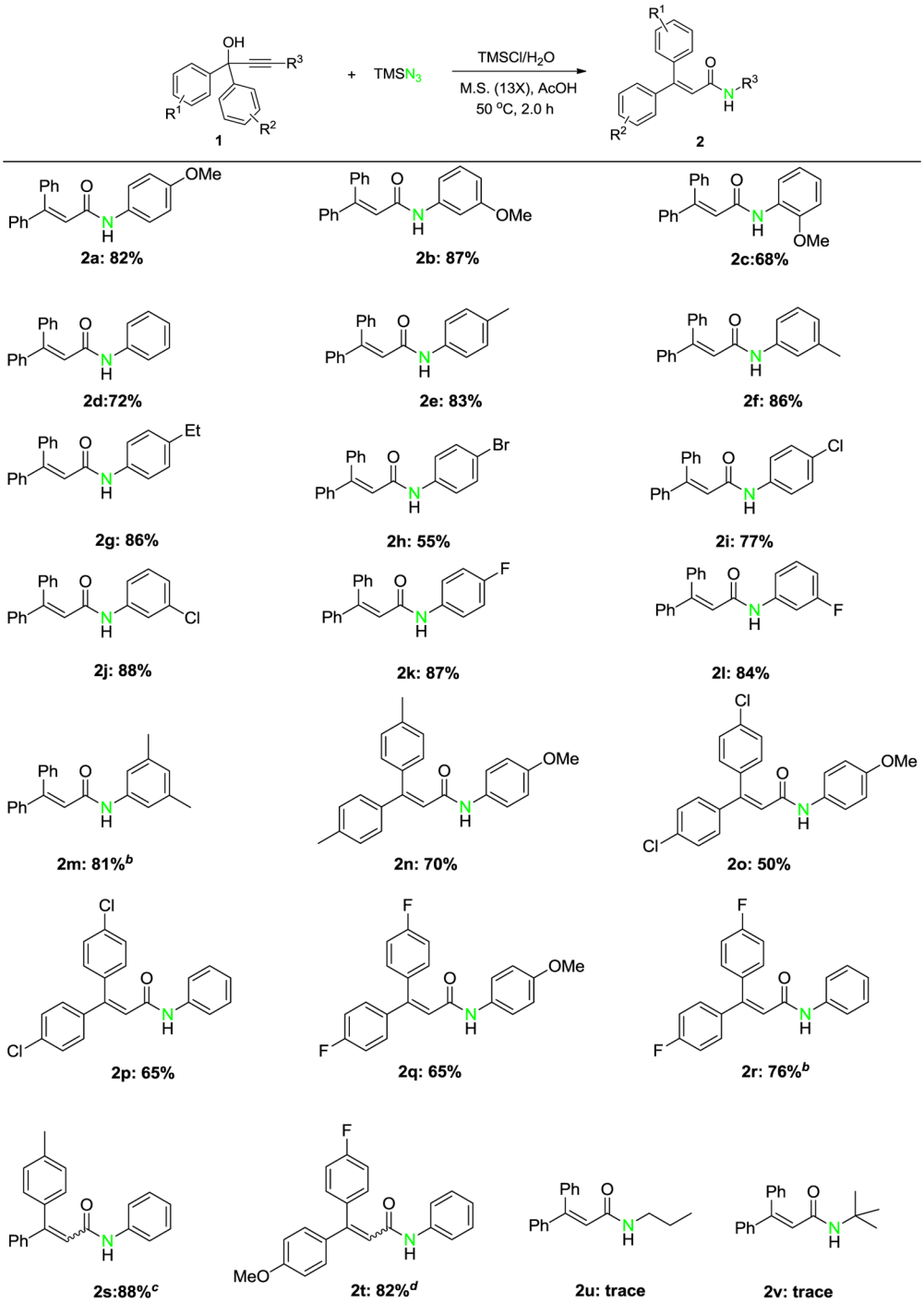
Table 2. Tranformation of Tertiary Propargylic Alcohols into α,β-Unsaturated Amides[a,b,c,d]



[a]Unless otherwise noted, all reactions were performed with 0.1 mmol of **1**, 0.4 mmol of $TMSN_3$, 2.0 equiv of H_2O, 3.0 equiv of TMSCl, and molecular sieves (13X; 30 mg) in CH_3COOH (1.0 mL) at 50 °C. [b]4.0 equiv of TMSCl was used. [c]The ratio of E/Z is 1.5:1. [d]The ratio of E/Z is 1.1:1.

promoter (Table 1). After treatment of a mixture of propargyl alcohol **1a** and $TMSN_3$ (2.0 equiv) with TMSCl (1.0 equiv) in the presence of H_2O (2.0 equiv) and 13X molecular sieves in MeCN for 2.0 h, the expected product *N*-(4-methoxyphenyl)-3,3-diphenylacrylamide **2a** was obtained in 35% yield along with the Meyer−Schuster rearrangement product[12] α,β-unsaturated ketone and tetrazoles[11] as the byproducts (entry 1). Then, a series of representative solvents were chosen for our study (entries 1−5), among which HOAc gave a better yield of 50% (entry 3).Toluene and 1,4-dioxane turned out to be ineffective for this reaction, and only a trace amount of the product could be obtained (entries 4 and 5). When the loading of $TMSN_3$ was increased to 3.0 equiv, the yield of **2a** could be further increased to 65% (entry 6). In contrast to TMSCl, other acid promoters, such as TFA, $BF_3{\cdot}Et_2O$, and *p*-TsOH, were unable to give satisfactory results (entries 7−9). It was found that the Meyer−Schuster rearrangement dominated the reaction in the presence of the above acids. To suppress this

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Scheme 2. Reaction of Tertiary Propargylic Alcohol 1w

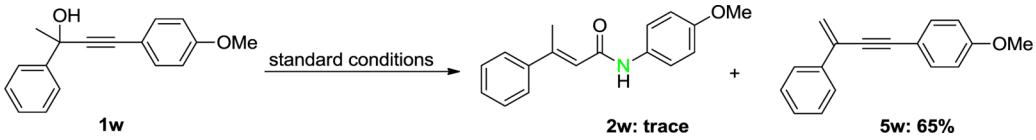
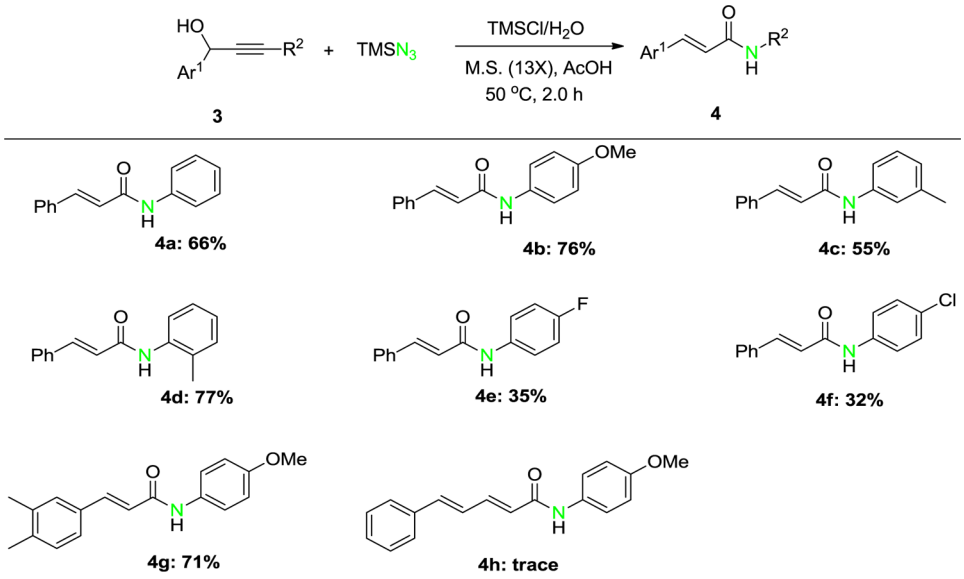


Table 3. Tranformation of Secondary Propargylic Alcohols into α,β-Unsaturated Amides[a]



[a]Unless otherwise noted, all reactions were performed with 0.2 mmol of **3** with 0.8 mmol of $TMSN_3$, 2.0 equiv of H_2O, 3.0 equiv of TMSCl, and molecular sieves (13X; 60 mg) in CH_3COOH (2.0 mL) at 50 °C.

side reaction, the loadings of TMSCl and $TMSN_3$ were increased again, and the yield of **2a** was further improved to 82% (entries 10-12). No higher yields could be obtained by adjusting the amount of water (entries 13-14). When the reaction was performed in the absence of molecular sieves, a poor yield of **2a** was obtained. This might due to the reason that molecular sieves (13X) served as a solid acid to activate the dehydration of propargylic alcohols (entry 15).[13] When 4 or 5 Å molecular sieves were applied in this reaction, no better yields were obtained (entries 16−17). Other sources of azides such as sodium azide and diphenylphosphoryl azide (DPPA) were also examined, which failed to give superior yields (entries 20 and 21). Consequently, $TMSN_3$ was confirmed as the most efficient nitrogen source. Taking into consideration that TMSCl may react with water to generate HCl along with TMSOH, we tested hydrochloric acid and AcCl, and the desired product **2a** could be obtained in moderate yields (entries 22 and 23). These results indicated that the HCl might be the real mediator to promote the dehydration of the propargyl alcohols.[14] Finally, the use of TMSCl (3.0 equiv) in the presence of H_2O (2.0 equiv) with $TMSN_3$ (4.0 equiv) in acetic acid at 50 °C was determined to be the optimal reaction conditions.[15]

With the optimized reaction conditions in hand, the substrate scope of this transformation was investigated (Table 2). Various tertiary propargyl alcohols **1a−t** were compatible with this protocol, and the corresponding products **2a−t** could be obtained in moderate to excellent yields. First, the influence of substituents on the aryl groups attached to the alkyne was examined. When electron-donating substituents (OMe, Me, Et) were attached on the *para*- or *meta*-positions, the reaction performed well and gave the desired products in good to excellent yields (**2a−b**, **2d−g**). When there was a substituent (OMe) on the *ortho*-position, the corresponding product was afforded in moderate yield (**2c**), indicating that the steric hindrance did not have much impact on the transformation reactivity. Halo-substituted propargyl alcohols (**1h−j**) worked well to produce the corresponding halo-substituted amides (**2h−j**), which might have potential applications in further coupling reactions. Moreover, substrates containing electron-withdrawing groups also gave the corresponding products in excellent yields (**2k−l**). It is worth noting that the substrate with two methyl substituents gave a satisfactory yield of 81% (**2m**). In addition, the other two aryl bearing electron-donating or electron-withdrawing groups (R^1, R^2) were well tolerated under the standard conditions, and the desired products were obtained in moderate to good yields (**2n−r**). When the unsymmetric propargyl alcohols such as 4-methylbenzo propargyl alcohol (**1s**) and 4-fluoro-4′-methoxyl propargyl alcohol (**1t**) were employed, two regioisomers were obtained with the regioselectivities of 1.5:1 and 1.1:1, respectively (**2s−t**).[16] However, alkyl-substituted tertiary propargylic alcohols **1u** and **1v** failed to afford the corresponding products **2u** and **2v** under the optimal conditions. This might due to the fact that the alkyl group could not migrate to the nitrogen atom in the rearrangement process.

When 1-methyl-1-phenyl-substituted tertiary propargylic alcohol **1w** was employed under the optimal conditions, only a 65% yield of 1,3-enyne compound **5w** was obtained and no desired product **2w** was detected (Scheme 2). It was thus established that the 1-methyl-1-phenyl-substituted tertiary propargylic alcohol **1w** was easier to go through an intra-

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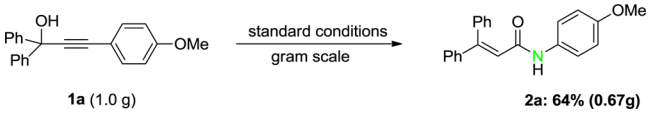
molecular dehydration in the presence of acid to afford the 1,3-enyne compound **5w**.[12a]

Various secondary propargylic alcohols **3a–h** were also prepared to examine the compatibility of this transformation under the optimal conditions (Table 3). Products with high regioselectivity were obtained in all cases. The electronic effect of the substituents on the aryl group attached to the alkyne was considerably clear; substrates bearing electron-donating substituents gave the results superior to those with electron-withdrawing ones (**4b–d** vs **4e–f**). Notably, substrate **3g** with two methyl substituents on the other aryl gave the expected product **4g** in 71% yield. To further extend the application of this transformation, substrate **3h** (*E*)-5-(4-methoxyphenyl)-1-phenylpent-1-en-4-yn-3-ol was also examined under the standard conditions. Unfortunately, the desired product **4h** was not observed.

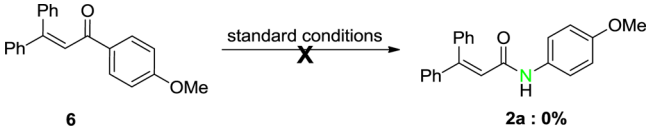
Noteworthily, when using easily prepared propargylic alcohol **1a** as the substrate to develop the efficiency of our method, a gram-scale reaction of **1a** could be performed under the standard conditions. The desired product **2a** was obtained in a moderate yield of 64%, which offered the potential application in organic synthesis (Scheme 3).

Scheme 3. Scale-Up Experiment



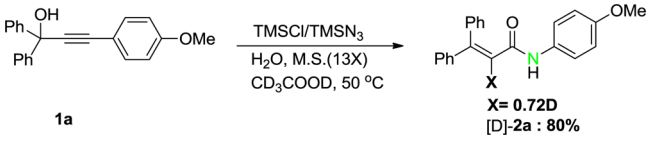
To explore the mechanism, a controlled experiment with a possible intermediate was investigated. As *α,β*-unsaturated ketones were detected as byproducts in this transformation, we assumed that one possible pathway is a tandem process involving a Lewis acid mediated Meyer–Schuster rearrangement[12] of propargylic alcohols, generating an *α,β*-unsaturated ketone, followed by a subsequent Schmidt reaction,[17] to form amides. To verify this possibility, the *α,β*-unsaturated ketone **6** was employed as the substrate under the standard conditions, but the desired product **2a** was not obtained (Scheme 4). This result indicated that the *α,β*-unsaturated ketone **6** was excluded as the intermediate in this novel transformation.

Scheme 4. Controlled Experiment



Furthermore, the source of a proton in intermediate **D** (see Scheme 6) was also examined. The reaction of **1a** in the presence of deuterium solvent (*d*-AcOH) produced the deuterated product [D]-**2a** in 80% yield (Scheme 5), which suggested that the proton source of intermediate **D** mainly came from the acetic acid.

Scheme 5. Labeling Experiment



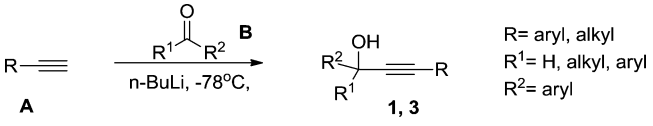
On the basis of the above detailed investigation and previous reports,[9–11] a plausible mechanism of this transformation is shown in Scheme 6. Initially, TMSCl may react with water to generate HCl along with TMSOH. Then, the hydrochloric acid promoted dehydration of propargyl alcohol **1** produces the propargyl cation **A**. Next, the substitution reaction of allenyl cation **B** generates allenylazide **C** in the presence of azide anion. The protolysis of intermediate **C** forms **D**, which could releases nitrogen gas through Schimidt-type rearrangement to afford the intermediate **F**. In this rearrangement process, the results with high chemoselectivity indicate that aryl groups have a greater migratory aptitude to the nitrogen atom than alkenyl groups. Subsequent nucleophilic attack by H_2O leads to the intermediate **G**. The desired *α,β*-unsaturated amides **2** could be afforded via a tautomerization of the intermediate **G**.

CONCLUSION

In conclusion, we have successfully developed an interesting method for the construction of *α,β*-unsaturated amides via a TMSCl-promoted reaction of propargyl alcohols with the commercially available $TMSN_3$ in the presence of H_2O. Various substituted *α,β*-unsaturated amides were obtained with high regioselectivity in moderate to excellent yields. This novel method goes through key allenylazide intermediates, followed by the Schimidt-type rearrangement, to afford the desired products. A nitrogenation process is achieved by the highly chemoselective $C_{sp}–C_{aryl}$ bond cleavage of propargyl alcohols. This method not only extends the applications of azides in organic chemistry but also provides a new and efficient synthetic strategy for the synthesis of *α,β*-unsaturated amides. Compared with the traditional HWE reaction[18] for the synthesis of *α,β*-unsaturated amides, our reaction can be carried out under mild conditions with good yields and avoids operational difficulties. Moreover, this reaction could be enlarged to gram scale in a satisfactory yield of 64%, which might display potential beneficial application in industrial production. Further studies are currently in progress in our group.

EXPERIMENTAL SECTION

General Procedure A: Synthesis of 1a–v, 3a–h According to Literature Procedures.[11] To a stirring solution of **A** (5 mmol) in



THF (1.0 M) was added dropwise *n*-BuLi (1.0 M in THF, 1.1 equiv) at −78 °C. Then, **B** (5 mmol) was added dropwise with stirring after 0.5 h. The solution was warming to room temperature after 1.0 h. After the reaction was completed as determined by TLC, the reaction mixture was quenched by addition of saturated aqueous ammonium chloride (20 mL) and extracted with ethyl acetate (3 × 20 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The crude material was purified by column chromatography on silica gel using petroleum ether/ethyl acetate to obtain the pure product propargylic acohols **1** or **3**. Compounds **1a**,[19a] **1c-i**,[19a] **1f**,[19b] **1g**,[19c] **1h**,[19b] **1i**,[19a] **1k**,[19a] **1m**,[19d] **1p**,[19a] **1r–s**,[19a] **1u**,[19e] **1v**,[19f] **1w**[19g] and **3a–f**,[19h] **3g**,[19i] and **3h**[19j] are known compounds.

General Procedure B: Synthesis of 2 and 4, 5v. The reaction of propargylic acohol **1a** (31.4 mg, 0.1 mmol), molecular sieves (13X, not

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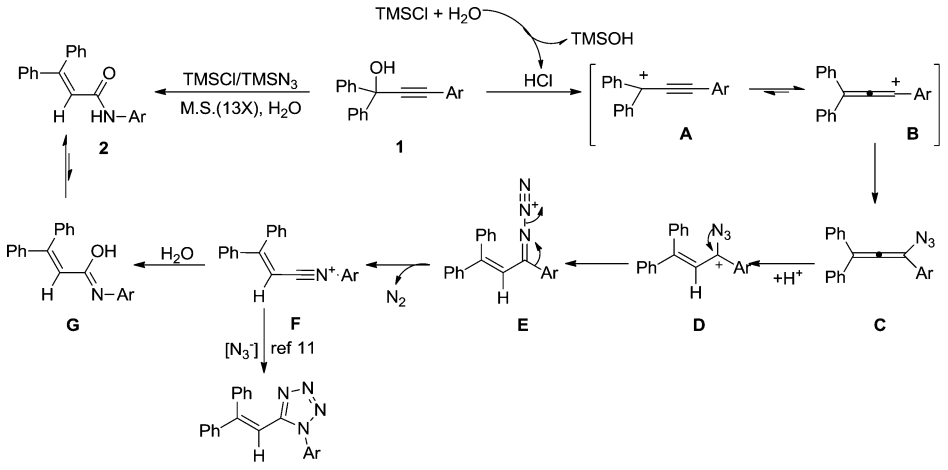
Scheme 6. Proposed Mechanism



activated) (30.0 mg), TMSCl (0.3 mmol), azidotrimethylsilane (0.4 mmol), and H_2O (0.2 mmol), in CH_3COOH (1.0 mL) was conducted at 50 °C under an air atmosphere. The reaction was complete within 2.0 h by TLC monitoring. The resulting mixture was cooled down to room temperature, and the appropriate amounts of water and ethyl acetate were added to the mixture (for the gram-scale reaction: the reaction mixture was directly concentrated under vacuum to remove most of the acetic acid, and the residual was added with appropriate amounts of water and ethyl acetate). Then, the organic phase was washed with saturated aqueous Na_2CO_3. The combined organic layers were washed with brine and dried over Na_2SO_4. The resultant product was then concentrated and purified by flash chromatography on silica gel to afford 27.1 mg of **2a**. Compounds **4a**,[5h] **4b**–**g**, and [20a] **6**[20b] are known compounds.

*3-(3-Methoxyphenyl)-1,1-diphenylprop-2-yn-1-ol (**1b**).* The resultant residue was purified by flash silica gel column chromatography (eluent:petroleum ether/EtOAc = 50:1, v/v) to afford **1b** as a colorless liquid (1.27 g, 81%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.47 (s, 1 H), 3.61 (s, 3 H), 6.81 (dd, J = 1.6 Hz, 8.4 Hz, 1 H), 6.96 (d, J = 0.8 Hz, 1 H), 7.04–7.08 (m, 1 H), 7.11–7.15 (m, 1 H), 7.17–7.21 (m, 2 H), 7.25–7.29 (m, 4 H), 7.64–7.66 (m, 4 H). ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 55.0, 74.5, 86.8, 91.5, 115.1, 116.4, 123.2, 124.2, 125.9, 127.5, 128.1, 129.2, 144.9, 159.0. HRMS (ESI, m/z): calcd for $C_{22}H_{18}O_2Na$: $[M + Na]^+$ = 337.1199; found: 337.1200. IR (neat, cm^{-1}): 3453, 3060, 2937, 2226, 1952, 1559, 1488, 1210, 1160, 1048, 992, 885, 773, 732, 643, 566, 528, 466.

*3-(3-Chlorophenyl)-1,1-diphenylprop-2-yn-1-ol (**1j**).* The resultant residue was purified by flash silica gel column chromatography (eluent:petroleum ether/EtOAc = 50:1, v/v) to afford **1j** as a yellow liquid (1.19 g, 75%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.18 (s, 1 H), 7.14 (t, J = 8.0 Hz, 1 H), 7.20–7.24 (m, 3 H), 7.27–7.31 (m, 5 H), 7.43 (s, 1 H), 7.61–7.63 (m, 4 H). ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 74.7, 85.6, 92.8, 123.9, 125.9, 127.7, 128.2, 128.8, 129.4, 129.8, 131.5, 134.0, 144.6. HRMS (ESI, m/z): calcd for $C_{21}H_{14}Cl$: $[M - H_2O + H]^+$ = 301.0779; found: 301.0777. IR (neat, cm^{-1}): 3429, 3062, 2925, 1950, 1592, 1449, 1163, 1044, 887, 767, 698, 643, 607, 561.

*3-(3-Fluorophenyl)-1,1-diphenylprop-2-yn-1-ol (**1l**).* The resultant residue was purified by flash silica gel column chromatography (eluent:petroleum ether/EtOAc = 50:1, v/v) to afford **1l** as a yellow liquid (1.17 g, 78%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.16 (s, 1 H), 6.98–7.03 (m, 1 H), 7.17 (dd, J = 1.6 Hz, 9.2 Hz, 1 H), 7.22–7.30 (m, 4 H), 7.32–7.34 (m, 4 H), 7.64 (d, J = 7.6 Hz, 4 H). ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 74.7, 85.8, 92.6, 115.9 (d, J = 21.0 Hz), 118.5 (d, J = 22.0 Hz), 124.1 (d, J = 9.0 Hz), 125.9, 127.6 (d, J = 3.0 Hz), 127.7, 128.3, 129.9 (d, J = 8.0 Hz), 144.7, 162.2 (d, J = 246.0 Hz). HRMS (ESI, m/z): calcd for $C_{21}H_{14}F$: $[M - H_2O + H]^+$ = 285.1074; found: 285.1068. IR (neat, cm^{-1}): 3429, 3062, 2926, 2230, 1951, 1607, 1580, 1487, 1150, 994, 873, 785, 735, 699, 563, 519, 461.

*3-(4-Methoxyphenyl)-1,1-di-p-tolylprop-2-yn-1-ol (**1n**).* The resultant residue was purified by flash silica gel column chromatography (eluent:petroleum ether/EtOAc = 50:1, v/v) to afford **1n** as a colorless liquid (1.40 g, 82%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.33 (s, 6 H), 2.78 (s, 1 H), 3.81 (s, 3 H), 6.84 (d, J = 8.8 Hz, 2 H), 7.14 (d, J = 8.0 Hz, 4 H), 7.43 (d, J = 8.8 Hz, 2 H), 7.54 (d, J = 8.0 Hz, 4 H). ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 21.1, 55.3, 74.6, 86.8, 90.6, 113.9, 114.6, 125.9, 128.9, 133.2, 137.3, 142.5, 159.8. HRMS (ESI, m/z): calcd for $C_{24}H_{21}O$: $[M - H_2O + H]^+$ = 325.1587; found: 325.1586. IR (neat, cm^{-1}): 3459, 2922, 2221, 1908, 1605, 1509, 1290, 1247, 1172, 1031, 991, 831, 736, 584, 548.

*1,1-Bis(4-chlorophenyl)-3-(4-methoxyphenyl)prop-2-yn-1-ol (**1o**).* The resultant residue was purified by flash silica gel column chromatography (eluent:petroleum ether/EtOAc = 50:1, v/v) to afford **1o** as a white solid (1.39 g, 73%); mp: 50–52 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.09 (s, 1 H), 3.78 (s, 3 H), 6.82–6.84 (m, 2 H), 7.23–7.30 (m, 4 H), 7.38–7.41 (m, 2 H), 7.53–7.57 (m, 4 H). ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 55.3, 73.9, 87.8, 89.3, 113.8, 114.0, 127.4, 128.4, 133.2, 133.7, 143.4, 160.0. HRMS (ESI, m/z): calcd for $C_{22}H_{15}Cl_2O$: $[M - H_2O + H]^+$ = 365.0494; found: 365.0493. IR (neat, cm^{-1}): 3406, 2933, 2222, 1903, 1703, 1605, 1509, 1402, 1250, 1172, 1091, 991, 901, 829, 737, 525.

*1,1-Bis(4-fluorophenyl)-3-(4-methoxyphenyl)prop-2-yn-1-ol (**1q**).* The resultant residue was purified by flash silica gel column chromatography (eluent:petroleum ether/EtOAc = 50:1, v/v) to afford **1q** as a white solid (1.33 g, 76%); mp: 66–68 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.95 (s, 1 H), 3.80 (s, 3 H), 6.85 (dd, J = 2.0, 6.8 Hz, 2 H), 6.99–7.04 (m, 4 H), 7.40–7.44 (m, 2 H), 7.58–7.63 (m, 4 H). ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 55.3, 73.9, 87.6, 89.8, 114.0 (d, J = 3.0 Hz), 115.1 (d, J = 12.0 Hz), 127.9 (d, J = 8.0 Hz), 133.2, 140.9 (d, J = 3.0 Hz), 160.0, 162.2 (d, J = 246.0 Hz). HRMS (ESI, m/z): calcd for $C_{22}H_{15}F_2O$: $[M - H_2O + H]^+$ = 333.1085; found: 333.1084. IR (neat, cm^{-1}): 3422, 2960, 2929, 2222, 1895, 1603, 1507, 1226, 1157, 1032, 832, 739, 581, 548.

*1-(4-Fluorophenyl)-1-(4-methoxyphenyl)-3-phenylprop-2-yn-1-ol (**1t**).* The resultant residue was purified by flash silica gel column chromatography (eluent:petroleum ether/EtOAc = 50:1, v/v) to afford **1t** as a white solid (1.15 g, 69%); mp: 64–66 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.98 (s, 1 H), 3.77 (s, 3 H), 6.86 (d, J = 8.8 Hz, 2 H), 7.01 (t, J = 8.8 Hz, 2 H), 7.30–7.33 (m, 3 H), 7.48–7.50 (m, 2 H), 7.55 (d, J = 8.4 Hz, 2 H), 7.61 (dd, J = 5.6 Hz, 8.4 Hz, 2 H). ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 55.2, 74.0, 87.1, 91.5, 113.6, 115.0 (d, J = 21.0 Hz), 122.2, 127.3, 127.8 (d, J = 8.0 Hz), 128.3, 128.7, 131.7, 137.1, 141.0 (d, J = 3.0 Hz), 159.1, 162.1 (d, J = 244.0 Hz). HRMS (ESI, m/z): calcd for $C_{22}H_{16}FO$: $[M - H_2O + H]^+$ = 315.1180; found: 315.1179. IR (neat, cm^{-1}): 3442, 3059, 2956, 2837, 2223, 1894, 1602, 1506, 1302, 1250, 1159, 1034, 987, 900, 838, 757, 738, 691, 585, 559, 524.

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*N-(4-Methoxyphenyl)-3,3-diphenylacrylamide (**2a**).* The resultant residue was purified by flash silica gel column chromatography (eluent:petroleum ether/EtOAc = 10:1, v/v) to afford **2a** as a white solid (27.1 mg, 82%); mp: 152−154 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.73 (s, 3 H), 6.50 (s, 1 H), 6.74 (d, J = 8.8 Hz, 2 H), 6.90 (s, 1 H), 7.03 (d, J = 8.8 Hz, 2 H), 7.31−7.35 (m, 7 H), 7.45−7.46 (m, 3 H). ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 55.4, 114.0, 121.3, 123.1, 128.0, 128.5, 128.9, 129.0, 129.1, 129.5, 130.7, 138.2, 140.6, 150.0, 156.3, 164.2. HRMS (ESI, m/z): calcd for $C_{22}H_{20}NO_2$: $[M + H]^+$ = 330.1489; found: 330.1483. IR (neat, cm^{-1}):3406, 3280, 2926, 2371, 2253, 1893, 1646, 1599, 1408, 1241,1172, 1038, 908, 836, 733, 649, 531, 455, 438.

*N-(3-Methoxyphenyl)-3,3-diphenylacrylamide (**2b**).* The resultant residue was purified by flash silica gel column chromatography (eluent:petroleum ether/EtOAc = 10:1, v/v) to afford **2b** as a white solid (28.7 mg, 87%); mp: 116−118 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.72 (s, 3 H), 6.49 (s, 1 H), 6.53−6.58 (m, 2 H), 6.92 (s, 1 H), 6.98 (s, 1 H), 7.07 (t, J = 8.0 Hz, 1 H), 7.28−7.35 (m, 7 H), 7.46−7.47 (m, 3 H). ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 55.2, 105.1, 110.0, 111.7, 123.0, 128.0, 128.5, 129.0, 129.0, 129.2, 129.4, 129.5, 138.1, 138.8, 140.4, 150.5, 160.0, 164.3. HRMS (ESI, m/z): calcd for $C_{22}H_{20}NO_2$: $[M + H]^+$ = 330.1489; found: 330.1479. IR (neat, cm^{-1}): 3400, 3303, 2929, 2248, 1954, 1658, 1540, 1293, 1158, 1035, 909, 734, 649, 580, 545, 455.

*N-(2-Methoxyphenyl)-3,3-diphenylacrylamide (**2c**).* The resultant residue was purified by flash silica gel column chromatography (eluent:petroleum ether/EtOAc = 10:1, v/v) to afford **2c** as a colorless liquid (22.5 mg, 68%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.59 (s, 3 H), 6.49 (s, 1 H), 6.72 (dd, J = 1.2, 8.0 Hz, 1 H), 6.87−6.98 (m, 2 H), 7.28−7.35 (m, 7 H), 7.40−7.42 (m, 3 H), 7.71 (s, 1 H), 8.40 (dd, J = 1.2, 8.0 Hz, 1 H). ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 55.3, 109.6, 119.6, 120.9, 123.3, 123.4, 127.7, 128.2, 128.4, 128.6, 129.0, 129.7, 138.1, 141.1, 147.7, 150.6, 164.2. HRMS (ESI, m/z): calcd for $C_{22}H_{20}NO_2$: $[M + H]^+$ = 330.1489; found: 330.1481. IR (neat, cm^{-1}): 3395, 2925, 2855, 2373, 1655, 1598, 1460, 1257, 1116, 908, 738, 700, 630, 462.

*N-3,3-Triphenylacrylamide (**2d**).* The resultant residue was purified by flash silica gel column chromatography (eluent:petroleum ether/EtOAc = 10:1, v/v) to afford **2d** as a white solid (21.6 mg, 72%); mp: 114−116 °C. ^{1}H NMR (400 MHz, CD_3COCD_3): δ 6.60 (s, 1 H), 7.01 (t, J = 7.6 Hz, 1 H), 7.22−7.28 (m, 4 H), 7.31−7.39 (m, 8 H), 7.54 (d, J = 7.6 Hz, 2 H), 9.00 (s, 1 H). ^{13}C{H} NMR (100 MHz, CD_3COCD_3): δ 120.0 120.1, 123.2, 123.3, 124.2, 128.8, 128.8, 128.9, 129.3, 129.5, 129.8, 130.5, 140.1, 140.4, 142.6, 152.3, 164.7. HRMS (ESI, m/z): calcd for $C_{21}H_{18}NO$: $[M + H]^+$ = 300.1383; found: 300.1378. IR (neat, cm^{-1}): 3406, 3311, 3057, 2926, 1955, 1655, 1598, 1441, 1313, 1265, 1177, 1029, 738, 699, 579, 510, 457.

*3,3-Diphenyl-N-(p-tolyl)acrylamide (**2e**).* The resultant residue was purified by flash silica gel column chromatography (eluent:petroleum ether/EtOAc = 10:1, v/v) to afford **2e** as a white solid (26.1 mg, 83%); mp: 154−156 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.25 (s, 3 H), 6.50 (s, 1 H), 6.90 (s, 1 H), 7.00 (s, 4 H), 7.30−7.35 (m, 7 H), 7.44−7.46 (m, 3 H). ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 20.8, 119.6, 123.2, 128.0, 128.5, 128.9, 129.0, 129.1, 129.3, 129.5, 133.7, 135.0, 138.2, 140.5, 150.2, 164.2. HRMS (ESI, m/z): calcd for $C_{22}H_{20}NO$: $[M + H]^+$ = 314.1539; found: 314.1535. IR (neat, cm^{-1}): 3404, 3293, 3056, 2924, 2248, 1655, 1600, 1517, 1404, 1313, 1243, 1182, 1029, 908, 733, 698, 649, 512, 453.

*3,3-Diphenyl-N-(m-tolyl)acrylamide (**2f**).* The resultant residue was purified by flash silica gel column chromatography (eluent:petroleum ether/EtOAc = 10:1, v/v) to afford **2f** as a white solid (27.0 mg, 86%); mp: 142−144 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.25 (s, 3 H), 6.49 (s, 1 H), 6.81−6.84 (m, 2 H), 6.94 (s, 1 H), 7.07 (t, J = 7.6 Hz, 2 H), 7.30−7.35 (m, 7 H), 7.45−7.47 (m, 3 H). ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 21.4, 116.6, 120.2, 123.1, 124.9, 128.0, 128.4, 128.6, 128.9, 129.0, 129.2, 129.5, 137.5, 138.1, 138.7, 140.5, 150.4, 164.3. HRMS (ESI, m/z): calcd for $C_{22}H_{20}NO$: $[M + H]^+$ = 314.1539; found: 314.1535. IR (neat, cm^{-1}): 3398, 3288, 2923, 2372, 1651, 1608, 1545, 1307, 1263, 1199, 1030, 908, 737, 696, 580, 555, 517, 456.

*N-(4-Ethylphenyl)-3,3-diphenylacrylamide (**2g**).* The resultant residue was purified by flash silica gel column chromatography (eluent:petroleum ether/EtOAc = 10:1, v/v) to afford **2g** as a white solid (28.2 mg, 86%); mp: 150−152 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.17 (t, J = 7.6 Hz, 3 H), 2.55 (q, J = 7.6 Hz, 2 H), 6.50 (s, 1 H), 6.92 (s, 1 H), 7.03 (s, 4 H), 7.31−7.35 (m, 7 H), 7.45−7.47 (m, 3 H). ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 15.6, 28.2, 119.7, 123.1, 128.0, 128.1, 128.5, 128.9, 129.0, 129.1, 129.5, 135.2, 138.2, 140.2, 140.5, 150.2, 164.2. HRMS (ESI, m/z): calcd for $C_{23}H_{22}NO$: $[M + H]^+$ = 328.1696; found: 328.1690. IR (neat, cm^{-1}): 3417, 2923, 1895, 1645, 1602, 1542, 1313, 1189, 1028, 908, 829, 744, 690, 614, 507, 453.

*N-(4-Bromophenyl)-3,3-diphenylacrylamide (**2h**).* The resultant residue was purified by flash silica gel column chromatography (eluent:petroleum ether/EtOAc = 10:1, v/v) to afford **2h** as a white solid (20.7 mg, 55%); mp: 190−192 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.49 (s, 1 H), 6.90 (s, 1 H), 7.00 (d, J = 8.8 Hz, 2 H), 7.28−7.37 (m, 9 H), 7.48 (t, J = 3.2 Hz, 3 H). ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 121.0, 122.7, 128.0, 128.5, 129.1, 129.4, 129.5, 131.8, 136.7, 138.0, 140.2, 150.9, 164.3. HRMS (ESI, m/z): calcd for $C_{21}H_{17}BrNO$: $[M + H]^+$ = 378.0488; found: 378.0482. IR (neat, cm^{-1}): 3308, 2926, 2252, 1893, 1655, 1597, 1530, 1307, 1243, 1183, 1070, 1006, 908, 826, 736, 698, 652, 585, 508, 460.

*N-(4-Chlorophenyl)-3,3-diphenylacrylamide (**2i**).* The resultant residue was purified by flash silica gel column chromatography (eluent:petroleum ether/EtOAc = 10:1, v/v) to afford **2i** as a white solid (25.6 mg, 77%); mp: 190−192 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.49 (s, 1 H), 6.95 (s, 1 H), 7.05 (d, J = 8.8 Hz, 2 H), 7.50 (d, J = 8.8 Hz, 2 H), 7.29−7.37 (m, 7 H), 7.47−7.48 (m, 3 H). ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 120.7, 122.7, 128.0, 128.5, 128.8, 129.0, 129.1, 129.4, 129.5, 136.2, 138.1, 140.2, 150.9, 164.3. HRMS (ESI, m/z): calcd for $C_{21}H_{17}ClNO$: $[M + H]^+$ = 334.0993; found: 334.0985. IR (neat, cm^{-1}): 3306, 2926, 2252, 1895, 1656, 1596, 1534, 1489, 1307, 1243, 1185, 1092, 908, 830, 736, 699, 511, 475, 409.

*N-(3-Chlorophenyl)-3,3-diphenylacrylamide (**2j**).* The resultant residue was purified by flash silica gel column chromatography (eluent:petroleum ether/EtOAc = 10:1, v/v) to afford **2j** as a white solid (29.3 mg, 88%); mp: 162−164 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.49 (s, 1 H), 6.88 (d, J = 8.0 Hz, 1 H), 6.99 (d, J = 8.0 Hz, 2 H), 7.10 (t, J = 8.0 Hz, 1 H), 7.29−7.37 (m, 8 H), 7.47−7.49 (m, 3 H). ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 117.4, 119.6, 122.5, 124.1, 128.1, 128.5, 129.1, 129.1, 129.4, 129.4, 129.7, 134.5, 138.0, 138.7, 140.2, 151.2, 164.3. HRMS (ESI, m/z): calcd for $C_{21}H_{17}ClNO$: $[M + H]^+$ = 334.0993; found: 334.0987. IR (neat, cm^{-1}): 3423, 2924, 2123, 1961, 1806, 1651, 1481, 1408, 1265, 1183, 1097, 907, 867, 738, 700, 580, 547, 457.

*N-(4-Fluorophenyl)-3,3-diphenylacrylamide (**2k**).* The resultant residue was purified by flash silica gel column chromatography (eluent:petroleum ether/EtOAc = 10:1, v/v) to afford **2k** as a white solid (27.6 mg, 87%); mp: 134−136 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.50 (s, 1 H), 6.88 (t, J = 8.8 Hz, 2 H), 6.96 (s, 1 H), 7.05−7.09 (m, 2 H), 7.29−7.36 (m, 7 H), 7.47 (t, J = 3.2 Hz, 3 H). ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 115.4 (d, J = 22.0 Hz), 121.2 (d, J = 8.0 Hz), 121.3, 122.7, 128.0, 128.5, 129.0, 129.3, 129.5, 133.6, 138.1, 140.3, 150.7, 159.2 (d, J = 242.0 Hz), 164.3. HRMS (ESI, m/z): calcd for $C_{21}H_{17}FNO$: $[M + H]^+$ = 318.1280; found: 318.1289. IR (neat, cm^{-1}): 3290, 3059, 2925, 2251, 1956, 1891, 1810, 1657, 1508, 1405, 1310, 1212, 908, 836, 733, 696, 650, 578, 513, 450.

*N-(3-Fluorophenyl)-3,3-diphenylacrylamide (**2l**).* The resultant residue was purified by flash silica gel column chromatography (eluent:petroleum ether/EtOAc = 10:1, v/v) to afford **2l** as a white solid (26.5 mg, 84%); mp: 130−132 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.49 (s, 1 H), 6.64−6.73 (m, 2 H), 7.02 (s, 1 H), 7.08−7.17 (m, 2 H), 7.29−7.37 (m, 7 H), 7.47−7.49 (m, 3 H). ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 107.0 (d, J = 26.0 Hz), 110.7 (d, J = 22.0 Hz), 114.6, 122.6, 128.0, 128.3, 128.5, 129.1 (d, J = 4.0 Hz), 129.4 (d, J = 6.0 Hz), 129.8, 129.9, 138.0, 139.1 (d, J = 11.0 Hz), 140.2, 151.1, 162.8 (d, J = 243.0 Hz), 164.3. HRMS (ESI, m/z): calcd for $C_{21}H_{17}FNO$: $[M + H]^+$ = 318.1280; found: 318.1285. IR (neat, cm^{-1}): 3404, 3263, 2923, 1954, 1806, 1656, 1601, 1489, 1262, 1202, 1076, 1030, 907, 867, 739, 697, 579, 549, 455.

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*N-(3,5-Dimethylphenyl)-3,3-diphenylacrylamide (**2m**).* The resultant residue was purified by flash silica gel column chromatography (eluent:petroleum ether/EtOAc = 10:1, v/v) to afford **2m** as a white solid (26.4 mg, 81%); mp: 174−176 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.20 (s, 6 H), 6.48 (s, 1 H), 6.66 (s, 1 H), 6.77 (s, 2 H), 6.97 (s, 1 H), 7.28−7.33 (m, 7 H), 7.44 (d, J = 2.0 Hz, 3 H). ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 21.3, 117.3, 123.0, 125.8, 128.0, 128.4, 128.8, 128.9, 129.1, 129.5, 137.4, 138.2, 138.4, 140.5, 150.4, 164.2. HRMS (ESI, m/z): calcd for $C_{23}H_{22}NO$: $[M + H]^+$ = 328.1696; found: 328.1690. IR (neat, cm^{-1}): 3302, 2920, 2251, 1956, 1652, 1617, 1326, 1207, 1031, 908, 841, 733, 698, 649, 582, 531, 455.

*N-(4-Methoxyphenyl)-3,3-di-p-tolylacrylamide (**2n**).* The resultant residue was purified by flash silica gel column chromatography (eluent:petroleum ether/EtOAc = 10:1, v/v) to afford **2n** as a faint yellow solid (25.0 mg, 70%); mp: 154−156 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.36 (s, 3 H), 2.42 (s, 3 H), 3.74 (s, 3 H), 6.44 (s, 1 H), 6.75 (d, J = 8.8 Hz, 2 H), 6.89 (s, 1 H), 7.04 (d, J = 8.8 Hz, 2 H), 7.12 (d, J = 8.4 Hz, 2 H), 7.18−7.27 (m, 6 H). ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 21.2, 21.3, 55.4, 114.0, 121.3, 122.0, 128.0, 129.1, 129.5, 129.6, 131.0, 135.3, 137.9, 138.8, 139.2, 150.2, 156.2, 164.5. HRMS (ESI, m/z): calcd for $C_{24}H_{24}NO_2$: $[M + H]^+$ = 358.1802; found: 358.1795. IR (neat, cm^{-1}): 3399, 3292, 2924, 2249, 1909, 1655, 1510, 1245, 1036, 908, 824, 733, 649, 521, 473.

*3,3-Bis(4-chlorophenyl)-N-(4-methoxyphenyl)acrylamide (**2o**).* The resultant residue was purified by flash silica gel column chromatography (eluent:petroleum ether/EtOAc = 10:1, v/v) to afford **2o** as a faint yellow solid (20.0 mg, 50%); mp: 200−202 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.76 (s, 3 H), 6.42 (s, 1 H), 6.79 (d, J = 8.8 Hz, 2 H), 6.95 (s, 1 H), 7.19 (dd, J = 8.8, 13.6 Hz, 4 H), 7.24 (d, J = 8.8 Hz, 3 H), 7.31 (d, J = 8.8 Hz, 2 H), 7.40 (d, J = 8.4 Hz, 2 H). ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 55.5, 114.2, 121.5, 123.1, 128.8, 129.0, 129.4, 130.5, 130.9, 135.1, 135.5, 136.3, 139.0, 148.7, 156.6, 163.6. HRMS (ESI, m/z): calcd for $C_{22}H_{18}Cl_2NO_2$: $[M + H]^+$ = 398.0709; found: 398.0701. IR (neat, cm^{-1}): 3281, 2927, 2254, 1728, 1648, 1611, 1544, 1442, 1408, 1312, 1240, 1174, 1088, 1011, 905, 831, 729, 650, 488, 428.

*3,3-Bis(4-chlorophenyl)-N-phenylacrylamide (**2p**).* The resultant residue was purified by flash silica gel column chromatography (eluent:petroleum ether/EtOAc = 10:1, v/v) to afford **2p** as a white solid (23.8 mg, 65%); mp: 180−182 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.43 (s, 1 H), 7.01 (s, 1 H), 7.05−7.09 (m, 1 H), 7.20 (d, J = 8.4 Hz, 2 H), 7.25 (d, J = 4.0 Hz, 6 H), 7.31−7.39 (m, 2 H), 7.40 (d, J = 8.4 Hz, 2 H). ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 119.7, 123.0, 124.5, 128.8, 129.0, 129.1, 129.4, 130.9, 135.2, 135.6, 136.2, 137.4, 138.9, 149.2, 163.7. HRMS (ESI, m/z): calcd for $C_{21}H_{16}Cl_2NO$: $[M + H]^+$ = 368.0603; found: 368.0596. IR (neat, cm^{-1}): 3422, 3293, 2925, 1904, 1781, 1653, 1543, 1490, 1439, 1311, 1264, 1187, 1090, 1014, 908, 827, 735, 549, 489.

*3,3-Bis(4-fluorophenyl)-N-(4-methoxyphenyl)acrylamide (**2q**).* The resultant residue was purified by flash silica gel column chromatography (eluent:petroleum ether/EtOAc = 10:1, v/v) to afford **2q** as a white solid (23.7 mg, 65%); mp: 158−160 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.75 (s, 3 H), 6.39 (s, 1 H), 6.78 (d, J = 8.8 Hz, 2 H), 6.95 (s, 1 H), 7.02 (d, J = 8.8 Hz, 2 H), 7.10−7.15 (m, 4 H), 7.22−7.31 (m, 4 H). ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 55.4, 114.1, 115.5 (d, J = 22.0 Hz), 115.9 (d, J = 21.0 Hz), 121.5, 122.7, 129.9 (d, J = 9.0 Hz), 130.0, 130.6, 131.4 (d, J = 8.0 Hz), 134.0, 136.8, 148.8, 156.5, 163.0 (d, J = 248.0 Hz), 163.4 (d, J = 249.0 Hz), 163.9. HRMS (ESI, m/z): calcd for $C_{22}H_{18}F_2NO_2$: $[M + H]^+$ = 366.1300; found: 366.1295. IR (neat, cm^{-1}): 3283, 2922, 2373, 1898, 1722, 1654, 1598, 1544, 1508, 1314, 1222, 1157, 1103, 1034, 919, 833, 739, 615, 524, 450.

*3,3-Bis(4-fluorophenyl)-N-phenylacrylamide (**2r**).* The resultant residue was purified by flash silica gel column chromatography (eluent:petroleum ether/EtOAc = 10:1, v/v) to afford **2r** as a white solid (25.5 mg, 76%); mp: 164−166 °C. ^{1}H NMR (400 MHz, CD_3COCD_3): δ 6.60 (s, 1 H), 7.02 (t, J = 7.6 Hz, 1 H), 7.10−7.17 (m, 4 H), 7.23−7.31 (m, 4 H), 7.34−7.38 (m, 2 H), 7.58 (d, J = 8.0 Hz, 2 H), 9.18 (s, 1 H). ^{13}C{H} NMR (100 MHz, CD_3COCD_3): δ 115.2 (d, J = 22.0 Hz), 115.8 (d, J = 22.0 Hz), 119.7 (d, J = 9.0 Hz), 123.0, 123.9, 129.2, 130.7 (d, J = 9.0 Hz), 132.2 (d, J = 8.0 Hz), 135.7 (d, J = 3.0 Hz), 138.5 (d, J = 4.0 Hz), 139.9, 150.2, 163.1 (d, J = 244.0 Hz), 163.7 (d, J = 246.0 Hz), 164.0. HRMS (ESI, m/z): calcd for $C_{21}H_{16}F_2NO$: $[M + H]^+$ = 336.1194; found: 336.1190. IR (neat, cm^{-1}): 3265, 2924, 2367, 1903, 1639, 1598, 1542, 1507, 1440, 1314, 1221, 1157, 1099, 837, 754, 696, 545, 528.

*N-3-Diphenyl-3-(p-tolyl)acrylamide (**2s**).* The resultant residue was purified by flash silica gel column chromatography (eluent:petroleum ether/EtOAc = 10:1, v/v) to afford **2s** as a white solid (27.6 mg, 88%); mp: 100−102 °C. HRMS (ESI, m/z): calcd for $C_{22}H_{20}NO$: $[M + H]^+$ = 314.1539; found: 314.1531. IR (neat, cm^{-1}): 3297, 2923, 2245, 1946, 1654, 1598, 1542, 1440, 1313, 1184, 1030, 908, 818, 754, 732, 694, 550, 478.

*(Z)-3-(4-Fluorophenyl)-3-(4-methoxyphenyl)-N-phenylacrylamide (**2t**).* The resultant residue was purified by flash silica gel column chromatography (eluent:petroleum ether/EtOAc = 10:1, v/v) to afford **2t** as a white solid (13.5 mg, 39%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.84 (s, 3 H), 6.36 (s, 1 H), 6.95−6.99 (m, 2 H), 7.02 (d, J = 8.4 Hz, 2 H), 7.09 (s, 1 H), 7.18−7.29 (m, 8 H). ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 55.4, 114.4, 115.4 (d, J = 22.0 Hz), 119.6, 122.3, 124.1, 128.8, 130.0 (d, J = 8.0 Hz), 131.1, 137.2, 137.7, 149.5, 160.3, 163.3 (d, J = 249.0 Hz), 164.4. HRMS (ESI, m/z): calcd for $C_{22}H_{19}FNO_2$: $[M + H]^+$ = 348.1394; found: 348.1390. IR (neat, cm^{-1}): 3295, 2927, 1895, 1652, 1599, 1510, 1440, 1313, 1248, 1179, 1032, 908, 833, 757, 734, 692, 548, 508.

*(E)-3-(4-Fluorophenyl)-3-(4-methoxyphenyl)-N-phenylacrylamide (**2t′**).* The resultant residue was purified by flash silica gel column chromatography (eluent:petroleum ether/EtOAc = 10:1, v/v) to afford **2t′** as a white solid (15.0 mg, 43%); mp: 128−130 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.82 (s, 3 H), 6.39 (s, 1 H), 6.85 (d, J = 8.8 Hz, 2 H), 7.03−7.09 (m, 2 H), 7.13 (d, J = 8.4 Hz, 2 H), 7.19−7.25 (m, 6 H), 7.28−7.32 (m, 2 H). ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 55.3, 113.9, 115.8 (d, J = 21.0 Hz), 119.5, 120.9, 124.1, 128.9, 129.5, 131.4 (d, J = 8.0 Hz), 133.0, 134.4, 137.7, 150.0, 160.7, 162.9 (d, J = 248.0 Hz), 164.3. HRMS (ESI, m/z): calcd for $C_{22}H_{19}FNO_2$: $[M + H]^+$ = 348.1394; found: 348.1390. IR (neat, cm^{-1}): 3295, 2927, 1895, 1652, 1599, 1510, 1440, 1313, 1248, 1179, 1032, 908, 833, 757, 734, 692, 548, 508.

*N-Phenylcinnamamide (**4a**).* The resultant residue was purified by flash silica gel column chromatography (eluent:petroleum ether/EtOAc = 10:1, v/v) to afford **4a** (29.5 mg, yield 66%). ^{1}H NMR (400 MHz, d-DMSO): δ 6.85 (d, J = 15.6 Hz, 1 H), 7.07 (t, J = 7.6 Hz, 1 H), 7.34 (t, J = 8.0 Hz, 2 H), 7.40−7.47 (m, 3 H), 7.58−7.64 (m, 3 H), 7.71 (d, J = 7.6 Hz, 2 H), 10.21 (s, 1 H). ^{13}C{H} NMR (100 MHz, d-DMSO): δ 119.2, 122.3, 123.3, 127.7, 128.8, 129.0, 129.7, 134.7, 139.2, 140.1, 163.5.

*N-(4-Methoxyphenyl)cinnamamide (**4b**).* The resultant residue was purified by flash silica gel column chromatography (eluent:petroleum ether/EtOAc = 10:1, v/v) to afford **4b** (38.4 mg, yield 76%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.74 (s, 3 H), 6.62 (d, J = 15.6 Hz, 1 H), 6.82 (d, J = 8.8 Hz, 2 H), 7.27−7.31 (m, 3 H), 7.40−7.42 (m, 2 H), 7.55 (d, J = 8.8 Hz, 2 H), 7.70 (d, J = 15.6 Hz, 1 H), 8.13 (s, 1 H). ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 55.5, 114.2, 121.2, 122.0, 127.9, 128.8, 129.8, 131.3, 134.8, 141.8, 156.6, 164.3.

*N-(m-Tolyl)cinnamamide (**4c**).* The resultant residue was purified by flash silica gel column chromatography (eluent:petroleum ether/EtOAc = 10:1, v/v) to afford **4c** as a colorless liquid (26.1 mg, yield 55%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.32 (s, 3 H), 6.58 (d, J = 15.6 Hz, 1 H), 6.93 (d, J = 7.6 Hz, 1 H), 7.19−7.25 (m, 1 H), 7.34−7.35 (m, 3 H), 7.41 (d, J = 6.8 Hz, 1 H), 7.48−7.49 (m, 3 H), 7.65 (s, 1 H), 7.74 (d, J = 15.6 Hz, 1 H). ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 21.5, 117.1, 120.7, 121.0, 125.3, 127.9, 128.8, 128.9, 129.9, 134.6, 138.0,139.0, 142.2, 164.1. IR (neat, cm^{-1}): 3296, 2922, 1947, 1659, 1611, 1548, 1490, 1448, 1342, 1261, 1205, 1090, 976, 863, 761, 687, 558, 489, 441.

*N-(o-Tolyl)cinnamamide (**4d**).* The resultant residue was purified by flash silica gel column chromatography (eluent:petroleum ether/EtOAc = 10:1, v/v) to afford **4d** as a white solid (36.4 mg, yield 77%); mp: 164−166 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.28 (s, 3 H), 6.62 (d, J = 15.6 Hz, 1 H), 7.08 (s, 1 H), 7.20 (t, J = 8.0 Hz, 2 H), 7.34−

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7.35 (m, 3 H), 7.43−7.48 (m. 3H), 7.73 (d, J = 15.2 Hz, 1 H), 7.88 (s, 1 H). $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ 17.8, 126.7, 127.9, 128.8, 128.9, 129.8, 130.5, 134.6, 135.7, 142.2, 164.2.

*N-(4-Fluorophenyl)cinnamamide (**4e**).* The resultant residue was purified by flash silica gel column chromatography (eluent:petroleum ether/EtOAc = 10:1, v/v) to afford **4e** as a white solid (16.8 mg, yield 35%); mp: 138−140 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 6.57 (d, J = 15.6 Hz, 1 H), 7.02 (t, J = 8.4 Hz, 2 H), 7.35−7.36 (m, 3 H), 7.48−7.50 (m, 2 H), 7.58 (s, 2 H), 7.68 (s, 1 H), 7.74 (d, J = 15.6 Hz, 1 H). $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ 115.7 (d, J = 18.0 Hz), 120.8, 121.9, 128.0, 129.0, 130.1, 134.0, 34.5, 142.5, 159.6 (d, J = 217.0 Hz), 164.1.

*N-(4-Chlorophenyl)cinnamamide (**4f**).* The resultant residue was purified by flash silica gel column chromatography (eluent:petroleum ether/EtOAc = 10:1, v/v) to afford **4f** as a white solid (16.5 mg, yield 32%); mp: 178−180 °C. ^1H NMR (400 MHz, CD_3COCD_3): δ 6.83 (d, J = 15.6 Hz, 1 H), 7.33−7.35 (m, 2 H), 7.37−7.43 (m, 3 H), 7.60−7.62 (m, 2 H), 7.70 (d, J = 15.6 Hz, 1 H), 7.81 (d, J = 8.8 Hz, 2 H), 9.52 (s, 1 H). $^{13}C\{H\}$ NMR (100 MHz, CD_3COCD_3): δ 121.5, 122.4, 128.4, 128.4, 129.3, 129.6, 130.4, 135.7, 139.1, 141.8, 164.3.

*(E)-3-(3,4-Dimethylphenyl)-N-(4-methoxyphenyl)acrylamide (**4g**).* The resultant residue was purified by flash silica gel column chromatography (eluent:petroleum ether/EtOAc = 10:1, v/v) to afford **4g** as a white solid (40.0 mg, yield 71%); mp: 130−132 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 2.21 (s, 3 H), 2.25 (s, 3 H), 3.76 (s, 3 H), 6.54 (d, J = 15.6 Hz, 1 H), 6.83 (d, J = 9.2 Hz, 2 H), 7.07 (d, J = 7.6 Hz, 1 H), 7.20 (d, J = 7.2 Hz, 2 H), 7.54 (d, J = 8.4 Hz, 2 H), 7.67 (d, J = 15.6 Hz, 1 H), 7.83 (s, 1 H). $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ 19.6, 19.7, 55.4, 114.1, 119.8, 121.8, 125.4, 129.2, 130.1, 131.4, 132.4, 137.0, 138.8, 142.0, 156.4, 164.3. HRMS (ESI, m/z): calcd for $C_{18}H_{20}NO_2$: $[M + H]^+$ = 282.1489; found: 282.1481. IR (neat, cm^{-1}): 3265, 2925, 2247, 1873, 1745, 1658, 1622, 1511, 1462, 1412, 1344, 1240, 1168, 1035, 980, 908, 829, 734, 551, 523, 438.

*1-(4-Methoxyphenyl)-3,3-diphenylprop-2-en-1-one (**6**).* The resultant residue was purified by flash silica gel column chromatography (eluent:petroleum ether/EtOAc = 10:1, v/v) to afford **6** as a yellow solid; ^1H NMR (400 MHz, $CDCl_3$): δ 3.78 (s, 3 H), 6.83 (d, J = 8.4 Hz, 2 H), 7.06 (s, 1 H), 7.16−7.18 (m, 2 H), 7.21−7.25 (m, 3 H), 7.34−7.35 (m, 5 H), 7.90 (d, J = 8.4 Hz, 2 H). $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ 55.3, 113.5, 124.3, 127.9, 128.1, 128.3, 128.4, 129.0, 129.6, 131.0, 131.1, 139.0, 141.4, 153.3, 163.2.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

General remarks and ^1H and ^{13}C NMR spectra of the products. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(14) Comparing with other acids, TMSCl would react with water and generate HCl, which might be the most effective in catalyzing this reaction. However, addition of concentrated hydrochloric acid directly

would bring excessive water to the reaction system, which would promote the generation of byproducts.

(15) After treatment of a mixture of propargyl alcohol **1a** and $TMSN_3$ (4.0 equiv) with TMSCl (3.0 equiv) in the presence of H_2O (4.0 equiv) and 13X molecular sieves (activated) in dry acetic acid at 50 °C for 2.0 h, the desired product **2a** was obtained in 80% yield, which is equal to the optimal reaction condition. Considering the convenience in experimental operation as well as the possibility for further industrial applications, the acetic acid and the molecular sieves were used without further treatment in this reaction. For details of the reagents, see the Supporting Information.

(16) The isomeric ratio of **2s**/**2s′** was determined by ^{1}H NMR spectroscopy; The isomeric ratio of **2t**/**2t′** was determined by isolated yield, and the double-bond geometry was determined by NOE experiment.

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