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Copper-Catalyzed Direct Transformation of Secondary Allylic and Benzylic Alcohols into Azides and Amides: An Efficient Utility of Azide as a Nitrogen Source

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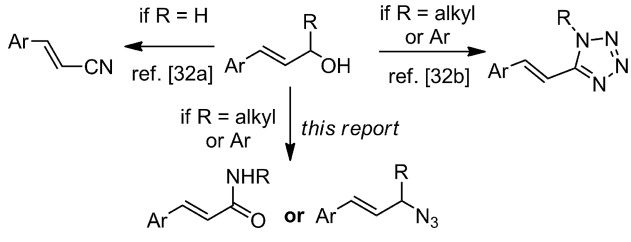
A mild and convenient method for the synthesis of amides has been explored by using secondary alcohols, $Cu(ClO_4)_2 \cdot 6H_2O$ as a catalyst, and trimethylsilyl azide ($TMSN_3$) as a nitrogen source in the presence of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) at ambient temperature. This method has been successfully adapted to the preparation of azides directly from their corresponding alcohols and offers excellent chemoselectivity in the formation of ω-halo azides and the azidation of allylic alcohols in the presence of a benzyl alcohol moiety. In addition, this strategy provides an opportunity to synthesize azides that can serve as precursors to β-amino acids.

Introduction

The construction of the carbon–nitrogen bond is an important transformation in organic synthesis because of its prevalence in a number of biologically active compounds. As a result, a large number of publications on this subject have appeared in recent years.[1–3] The amide functionality is the crucial backbone of peptide chemistry and serves as an important precursor in a variety of organic transformations. Amides have been used as coupling partners in various transition-metal-catalyzed coupling reactions such as those with aryl boronic acids or aryl halides,[4] and amides can be reduced into their amines[5] or hydrolyzed into acids.[6] In recent times, amides have been employed as directing groups in C–H functionalization strategies.[7] Traditionally, amides are synthesized by coupling carboxylic acids and carboxylic acid derivatives with an amine.[8,9] Amides can also be accessed through a Beckmann rearrangement,[10] a Schmidt rearrangement,[11] the oxidative amidation of alcohols,[12–14] aldehydes,[15,16] ketones,[17] and amines,[18] and the aminocarbonylation of aromatic halides.[19,20] Amides can also be synthesized by coupling aldehyde groups with amines,[21] azides,[22] or amides[23] under metal or metal-free reaction conditions. Usually, most of the above-mentioned methods utilize an amine as a coupling partner.

Similar to amides, organic azides are also important precursors in organic synthesis.[24,25] The utility of azides has been greatly enhanced by the development of click chemistry.[26] Apart from this, azides have also been used for the insertion of a nitrogen atom into a hydrocarbon unit to obtain nitriles,[27] tetrazoles,[28] and amides.[29,30] Recently, Jiao and co-workers reported an interesting method to synthesize amides and acrylamides from benzyl-substituted hydrocarbons under $FeCl_2$ catalysis.[30] Although this method is attractive, it involves starting materials that are not easy to access and require multistep synthetic sequences.[31] Recently, we reported the oxidative conversion of alcohols into their nitriles[32a] and tetrazoles (Scheme 1).[32b] During these investigations, it was observed that the corresponding azides were formed as an intermediate, which underwent further oxidation in the presence of DDQ (2,3-dichloro-5,6-dicyano-*p*-benzoquinone) to generate a nitrilium intermediate.[32] With this observation and in continuation of our work on the utility of azides,[32,33] we have synthesized amides directly from secondary alcohols, which are easily accessible or prepared by the reduction of ketones or the 1,2-addition of Grignard reagents to aldehydes. By using the present strategy, the successful chemoselective syntheses of ω-halo azides and ω-hydroxy azides have also been explored.



Scheme 1. Previous work.

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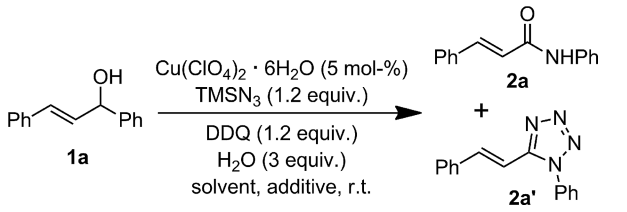
Results and Discussion

Synthesis of Amides

In search of suitable conditions to obtain an amide, we began by examining the reaction between (*E*)-1,3-diphenylprop-2-en-1-ol (**1a**) and trimethylsilyl azide ($TMSN_3$, 1.2 equiv.) with DDQ (1.2 equiv.) as the oxidant, $Cu(ClO_4)_2{\cdot}6H_2O$ as the catalyst, and water (3 equiv.) as an additive in dichloromethane (DCM) at room temperature (Table 1).[29] Surprisingly, this reaction resulted in the formation of tetrazole **2a′** as the sole product, and the formation of amide **2a** was not observed, even in trace amounts (Table 1, Entry 1, determined by ^1H NMR conversion). Changing the solvent from DCM to CH_3CN did not provide better results (Table 1, Entries 2 and 3,). However, to our delight, the use of acidic additives such as acetic acid (3 equiv.) was encouraging, and the expected amide **2a** was obtained in 30% yield along with tetrazole **2a′** (70% yield) as a major product (Table 1, Entry 4). Increasing the amount of AcOH to 10 equiv. was not useful, as the reaction furnished a mixture of amide **2a** and tetrazole **2a′** in a 50:50 ratio (Table 1, Entry 5). Remarkably, using acetic acid as the solvent gave a favorable result and furnished the expected amide **2a** as the sole product (Table 1, Entry 6). Therefore, the optimal reaction conditions for the efficient oxidative transformation of alcohols into their corresponding amides involved the combination of $Cu(ClO_4)_2{\cdot}6H_2O$ (5 mol-%), $TMSN_3$ (1.2 equiv.), DDQ (1.2 equiv.), and H_2O (3 equiv.) in AcOH as the solvent at ambient temperature.

Table 1. Optimization studies.[a]

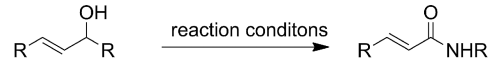


Entry	Solvent	Additive [equiv.]	Product[b]
1	CH_2Cl_2	none	**2a′** only
2	CH_3CN	none	complex mixture
3	CH_3CN	AcOH (3)	complex mixture
4	CH_2Cl_2	AcOH (3)	**2a** + **2a′** (30:70)
5	CH_2Cl_2	AcOH (10)	**2a** + **2a′** (50:50)
6	AcOH	none	**2a** only

[a] Reagents and conditions: **1a** (0.5 mmol), $TMSN_3$ (0.6 mmol), $Cu(ClO_4)_2{\cdot}6H_2O$ (0.025 mmol), DDQ (0.6 mmol), H_2O (1.5 mmol), additive, and solvent (2 mL) at room temp. for 1 h. [b] Products determined by ^1H NMR conversion.

After the optimization studies were complete, the substrate scope was studied by using a variety of secondary allylic alcohols, and the results are summarized in Tables 2 and 3. As shown in Table 2, secondary allylic alcohols that are substituted with identical aromatic rings at the 1- and 3-positions (i.e., **1a**–**1h**) furnished the expected acrylamides (i.e., **2a**–**2h**) in good to excellent yields (Table 2, Entries 1–8). Under the optimal reaction conditions, (*E*)-1,3-diphenylprop-2-en-1-ol (**1a**) furnished amide **2a** in 93% yield (Table 2, Entry 1). Alcohols that contain electron-donating substituents such as 4-methoxy and 4-methyl on the aryl ring furnished the corresponding amides **2b** and **2f** in 56 and 72% yield, respectively (Table 2, Entries 2 and 6). Substrates with a halide substituent such as a 4-bromo, 4-chloro, 4-fluoro, 2-bromo and 2-fluoro group on the aryl ring under the optimized reaction conditions furnished the corresponding amides **2c-2e, 2g** and **2h** in good to excellent yields (Table 2, Entries 3–5, 7 and 8).

Table 2. Substrate scope.[a,b]



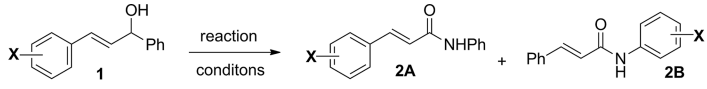
1 **2**

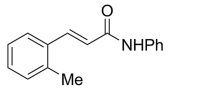
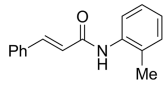
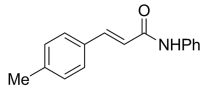
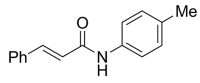
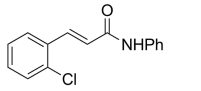
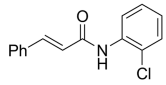
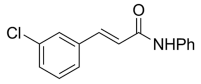
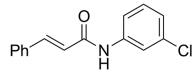
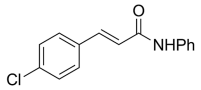
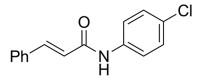
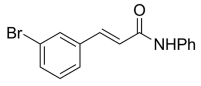
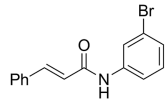
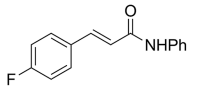
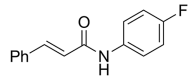
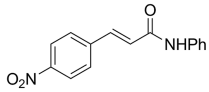
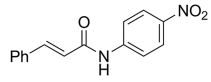
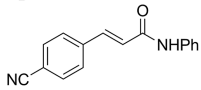
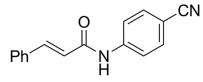
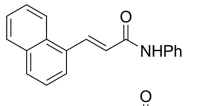
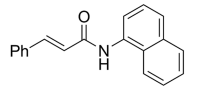
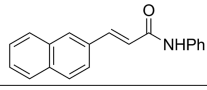
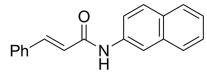
Entry	Substrate	Product	Yield (%)
1	**1a**	**2a**	93
2	**1b**	**2b**	56
3	**1c**	**2c**	88
4	**1d**	**2d**	72
5	**1e**	**2e**	91
6	**1f**	**2f**	72
7	**1g**	**2g**	71
8	**1h**	**2h**	86

[a] Reagents and conditions: **1** (0.5 mmol), $TMSN_3$ (0.6 mmol), $Cu(ClO_4)_2{\cdot}6H_2O$ (0.025 mmol), DDQ (0.6 mmol), H_2O (1.5 mmol), and AcOH (2 mL) at room temp. for 1 h. [b] Isolated yield.

The substrate scope was further investigated by using secondary allylic alcohols with different aryl moieties at the 3-position and a phenyl group at the 1-position. As expected, under the optimal conditions, these reactions furnished regioisomeric mixtures of the corresponding amides. Here, the regioselectivity of the reaction was determined by the electronic and steric factors associated with the substrate. Alcohol **1i** with a methyl substituent at the *ortho* position furnished amide **2i** as a mixture of regioisomers in a 67:33 ratio (78% yield, Table 3, Entry 1). However, alcohol **1j** with a methyl substituent at the *para* position of the aryl ring furnished amide **2j** in 66% yield as a mixture of regioisomers in a 27:73 ratio (Table 3, Entry 2). The effect on

Table 3. Substrate scope.[a,b]

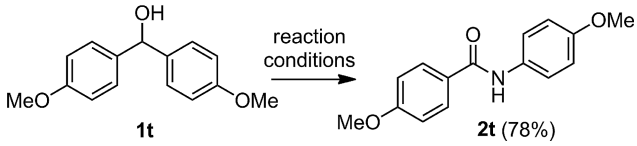


Entry	X	Product **A**	Product **B**	Yield (%) (**A**:**B**)
1	**1i**, 2-Me			78 **2i** (67:33)
2	**1j**, 4-Me			66 **2j** (27:73)
3	**1k**, 2-Cl			91 **2k** (50:50)
4	**1l**, 3-Cl			79 **2l** (35:65)
5	**1m**, 4-Cl			91 **2m** (50:50)
6	**1n**, 3-Br			91 **2n** (33:67)
7	**1o**, 4-F			81 **2o** (50:50)
8	**1p**, 4-NO_2			84 **2p** (75:25)
9	**1q**, 4-CN			45 **2q** (88:12)
10	**1r**, 1-naphthyl			73 **2r** (50:50)
11	**1s**, 2-naphthyl			90 **2s** (27:73)

[a] Reagents and conditions: **1** (0.5 mmol), $TMSN_3$ (0.6 mmol), $Cu(ClO_4)_2 \cdot 6H_2O$ (0.025 mmol), DDQ (0.6 mmol), H_2O (1.5 mmol), and AcOH (2 mL) at room temp. for 1 h. [b] Isolated yield.

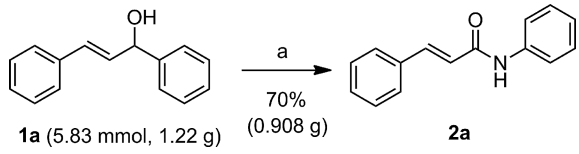
the regioselectivity of the reaction was then studied by having a chloro substituent at different positions of the aryl ring. Alcohol **1** that contains a chloro substituent at the *ortho* or *para* position of the aryl ring (i.e., **1k** and **1m**) furnished the corresponding amides **2k** and **2m** as a 50:50 mixture of regioisomers in 91% yield (Table 3, Entries 3 and 5). However, alcohol **1l** that contains a chloro substituent at the *meta* position yielded amide **2l** as a 35:65 mixture of regioisomers (79% yield, Table 3, Entry 4). Alcohol **1n** that contains a bromo substituent at the *meta* position of the aryl ring furnished amide **2n** in a 33:67 ratio of isomers (91% yield, Table 3, Entry 6). Alcohol **1o** with a fluoro substitution at the *para* position of the aryl ring did not have much impact and afforded the corresponding amide **2o** as a 50:50 regioisomeric mixture (81% yield, Table 3, Entry 7). Additionally, alcohols **1p** and **1q** that contain an electron-withdrawing substituent at the *para* position of the aryl ring furnished the corresponding amides **2p** and **2q** in a regioisomeric ratio of 75:25 and 88:12, respectively (Table 3, Entries 8 and 9). Finally, alcohols that have a naphthyl group such as (*E*)-3-(naphthalen-1-yl)-1-phenylprop-2-en-1-ol and (*E*)-3-(naphthalen-2-yl)-1-phenylprop-2-en-1-ol furnished the corresponding amides **2r** and **2s** in good yields (73 and 90%) with regioisomeric ratios of 50:50 and 27:73, respectively (Table 3, Entries 10 and 11).

Under the optimal reaction conditions, a symmetrical secondary benzyl alcohol such as bis(4-methoxyphenyl) methanol (**1t**) also afforded the corresponding amide **2t** in 78% yield (Scheme 2). However, substrates such as an allylic-alkylic or a benzylic-alkylic alcohol were treated under present reaction conditions but unfortunately failed to give the expected amide.



Scheme 2. Reaction with benzylic alcohol. Reagents and conditions: **1t** (0.5 mmol), $TMSN_3$ (0.6 mmol), $Cu(ClO_4)_2{\cdot}6H_2O$ (0.025 mmol), DDQ (0.6 mmol), H_2O (1.5 mmol), and AcOH (2 mL) at room temp. for 1 h.

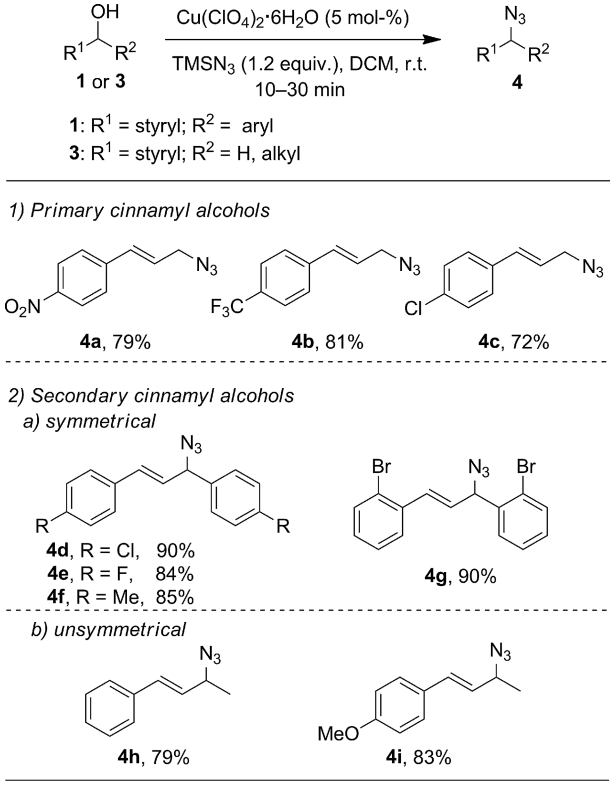
A further application of this methodology has been shown by carrying out the reaction on a preparative scale. Under the present reaction conditions, alcohol **1a** (1.22 g) furnished the expected amide **2a** in 70% yield (Scheme 3).



Scheme 3. Application on a preparative scale. Reagents and conditions: (a) **1a** (1.22 g, 5.83 mmol), $TMSN_3$ (1.2 equiv.), $Cu(ClO_4)_2{\cdot}6H_2O$ (5 mol-%), DDQ (1.2 equiv.), H_2O (3 equiv.), and AcOH (10 mL) at room temp. for 1 h.

Synthesis of Azides

Azides are important precursors and intermediates for a variety of organic transformations, and the present study offers an opportunity to synthesize azides directly from alcohols (Scheme 1). Therefore, we proceeded to investigate the synthesis of a variety of azides (Scheme 4). Generally, aliphatic azides are prepared by the nucleophilic substitution reaction of organic halides/mesylates/tosylates with sodium azide,[24] whereas aromatic azides are synthesized by using the classical Sandmeyer reaction. Apart from these, there have recently been a few reports on the synthesis of azides from the benzyl methyl ether and unsymmetrical dibenzyl ethers that are derived from secondary or tertiary benzyl alcohols[34] and benzylic silyl ethers.[35] There are also some reports about the azidation of alcohols.[36]



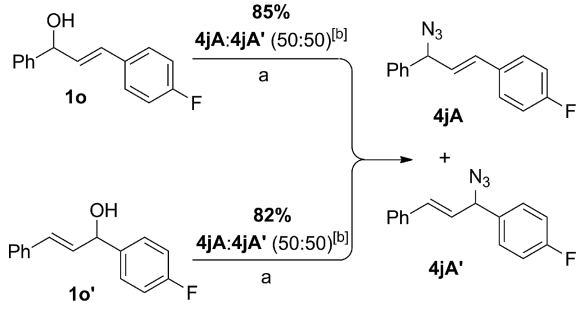
Scheme 4. Direct azidation of cinnamyl alcohols.

The aforementioned methods suffer from disadvantages such as the need of additional steps to synthesize the starting materials or the lack of a broad substrate scope. Because of these reasons and the significance of azides as intermediates in organic synthesis, there is a need to develop efficient methods for the synthesis of azides. In our earlier work[32] on the direct oxidative transformation of an alcohol into a nitrile, we observed the formation of an azide as an intermediate. It was surprising to see that highly Lewis acidic copper salts such as $Cu(ClO_4)_2{\cdot}6H_2O$ and $Cu(OTf)_2$ (OTf = trifluoromethanesulfonate) were effective catalysts, whereas other copper catalysts such as CuCl, CuBr, CuI, and $Cu(OAc)_2{\cdot}H_2O$ were detrimental to this reaction.

On the basis of our earlier work,[32] we established that $Cu(ClO_4)_2{\cdot}6H_2O$ (5 mol-%) and $TMSN_3$ (1.2 equiv.) in CH_2Cl_2 at ambient temperature were the optimal reaction conditions for the direct conversion of alcohols into azides. Initially, primary cinnamyl alcohol derivatives such as (*E*)-3-(4-nitrophenyl)prop-2-en-1-ol (**3a**), (*E*)-3-[4-(trifluoromethyl)phenyl]prop-2-en-1-ol (**3b**), and (*E*)-3-(4-chlorophenyl)prop-2-en-1-ol (**3c**), which have nitro, trifluoromethyl, and chloro substituents at the *para* position of the phenyl ring, were subjected to the reaction under optimal reaction conditions. In these cases, the reactions led to the formation of the corresponding azides **4a**, **4b**, and **4c**, respectively, in good to excellent yields (79, 81, and 72%, respectively). Furthermore, under the optimized reaction conditions, secondary cinnamyl alcohol derivatives such as (*E*)-1,3-bis(4-chlorophenyl)prop-2-en-1-ol (**1d**), (*E*)-1,3-bis(4-fluorophenyl)prop-2-en-1-ol (**1e**), (*E*)-1,3-di-*p*-tolylprop-2-en-1-ol (**1f**), and (*E*)-1,3-bis(2-bromophenyl)prop-2-en-1-ol (**1g**) that have chloro, fluoro, methyl, and bromo substituents on both aromatic rings of the alcohol yielded the corresponding azides **4d**, **4e**, **4f**, and **4g** in 90, 84, 85, and 90%, respectively. In addition, alcohols such as (*E*)-4-phenylbut-3-en-2-ol (**3h**) and (*E*)-4-(4-methoxyphenyl)but-3-en-2-ol (**3i**) furnished azides **4h** and **4i**, respectively, as the sole product, which can be explained by the extended stabilization of the carbocation by the cinnamyl moiety (Scheme 4).

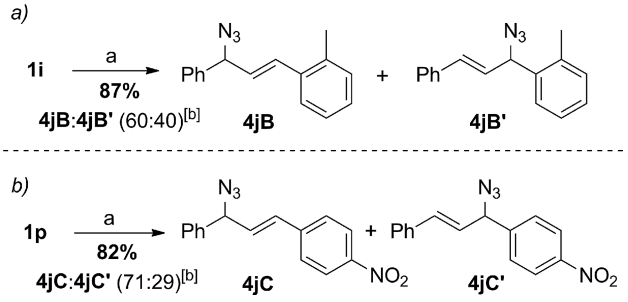
Alcohols (*E*)-3-(4-fluorophenyl)-1-phenylprop-2-en-1-ol (**1o**) and (*E*)-1-(4-fluorophenyl)-3-phenylprop-2-en-1-ol (**1ó**), which are regioisomers, were subjected to the optimal azidation conditions. Under these conditions, these isomeric alcohols furnished the isomeric mixture of azides **4jA** and **4jA′** in the same ratio (50:50) in good yields (Scheme 5). This clearly indicates that reaction of both alcohols **1o** and **1o′** proceeds through a similar intermedi-

ate, namely, the delocalized carbocation followed by the attack of $TMSN_3$ to give azides **4jA** and **4jA′** as shown in Scheme 5.



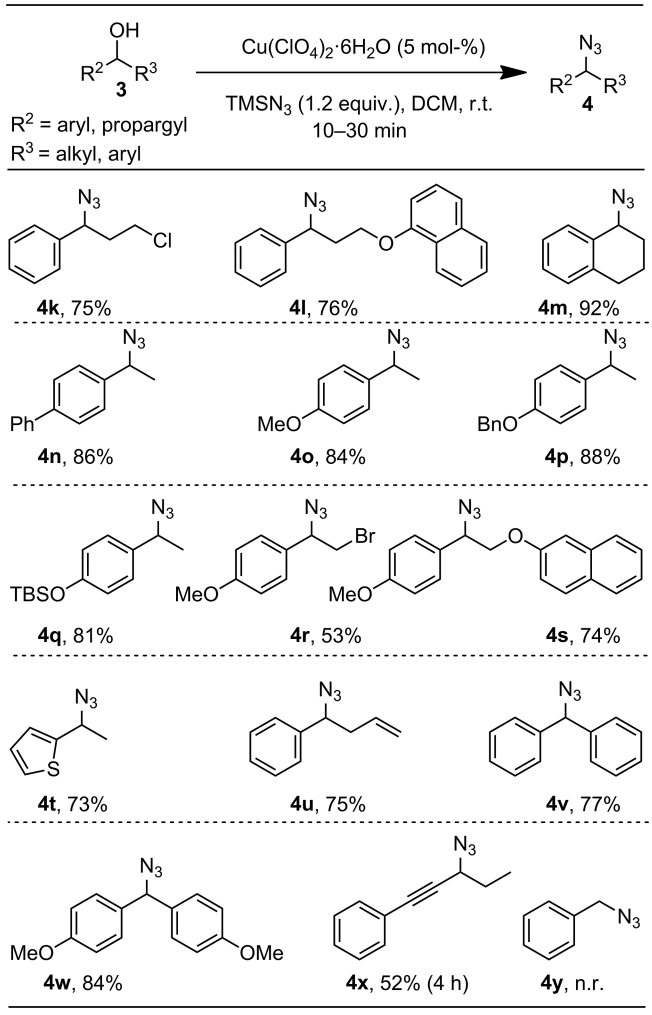
Scheme 5. Substrate scope. [a] Reagents and conditions: **1o** or **1o′** (0.5 mmol), $TMSN_3$ (0.6 mmol), $Cu(ClO_4)_2{\cdot}6H_2O$ (0.025 mmol), and dichloromethane (2 mL) at room temp. for 5–10 min. [b] Based on ^1H NMR conversion.

Furthermore, alcohols **1i** and **1p** were subjected to the azidation reaction, which furnished the corresponding mixture of azides **4jB/4jB′** in 60:40 ratio and **4jC/4jC′** in 71:29 ratio (Scheme 6, a and b), which are also in agreement with the amide ratios observed in Table 3, Entries 1 and 8.



Scheme 6. Substrate scope. [a] Reagents and conditions: **1i** or **1p** (0.5 mmol), $TMSN_3$ (0.6 mmol), $Cu(ClO_4)_2{\cdot}6H_2O$ (0.025 mmol), and AcOH (2 mL) at room temp. for 5–10 min. [b] Based on ^1H NMR conversion.

Then, the scope of this azidation reaction was extended to benzylic alcohols, and the results are summarized in Scheme 7. A variety of benzylic alcohols with different substituents underwent a facile transformation into their corresponding azides in good to excellent yields. 3-Chloro-1-phenylpropan-1-ol (**3k**), 3-(naphthalen-1-yloxy)-1-phenylpropan-1-ol (**3l**), 1,2,3,4-tetrahydronaphthalen-1-ol (**3m**), and 1-([1,1′-biphenyl]-4-yl)ethan-1-ol (**3n**) under the optimal reaction conditions furnished the corresponding azides **4k**, **4l**, **4m**, and **4n** in good to excellent yields. Electron-donating substituents on aromatic secondary alcohols such as 1-(4-methoxyphenyl)ethan-1-ol (**3o**), 1-(4-[benzyloxy]phenyl)ethan-1-ol (**3p**), and 1-{4-[(*tert*-butyldimethylsilyl)oxy]phenyl}ethan-1-ol (**3q**) underwent a facile transformation to yield the corresponding azides **4o**, **4p**, and **4q** in 84, 88, and 81% yield, respectively. Furthermore, 2-bromo-1-(4-methoxyphenyl)ethan-1-ol (**3r**) under the similar reaction conditions afforded the corresponding azide **4r** in a moderate yield (53%). It is noteworthy that halo-substituted alcohols such as **3k** and **3r**, which contain chloro and bromo substituents on a sp^3-hybridized carbon atom, exhibited excellent chemoselectivity and furnished the corresponding halo azides **4k** and **4r** in 75 and 53% yield, respectively.

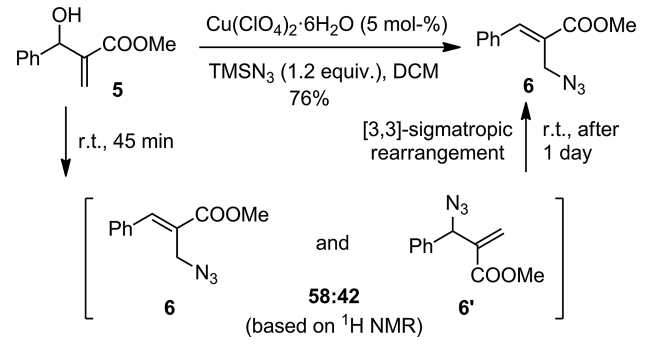


Scheme 7. Direct azidation of benzylic alcohols (TBS = *tert*-butyldimethylsilyl, n.r.: no reaction).

The chemoselectivity that was observed in the formation of the halo azides is rare and difficult to achieve. Further investigations showed that the reaction is versatile as 1-(4-methoxyphenyl)-2-(naphthalen-2-yloxy)ethan-1-ol (**3s**), 1-(thiophen-2-yl)ethan-1-ol (**3t**), and 1-phenylbut-3-en-1-ol (**3u**) furnished the corresponding azides **4s**, **4t**, and **4u** in good yields (74, 73, and 75%, respectively). Secondary symmetrical benzylic alcohols such as diphenylmethanol (**3v**) and 4,4′-bis(4-methoxyphenyl)methanol (**3w**) underwent smooth transformation to furnish the corresponding azides **4v** and **4w** in 77 and 84% yield, respectively. Under the reaction conditions, the alcohol with a propargyl moiety such as 1-phenylpent-1-yn-3-ol (**3x**) afforded the expected propargyl azide **4x** in 52% yield. However, primary benzyl alcohol (**3y**) did not undergo the reaction, and the corresponding benzyl azide (**4y**) was not obtained (Scheme 7).

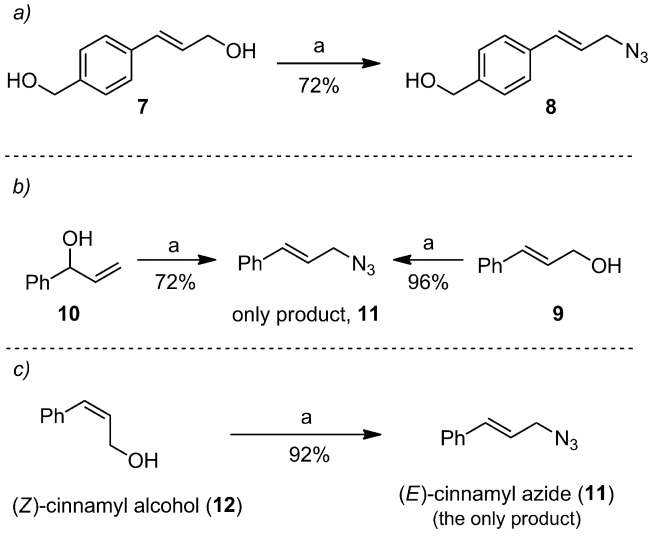
Methyl 2-[hydroxy(phenyl)methyl]acrylate (**5**), an alcohol derived from the Baylis–Hilmann reaction of methyl acryl-

ate with benzaldehyde, smoothly underwent the reaction to provide the regioisomeric mixture of the corresponding azides **6** and **6′** in a 58:42 ratio. It was found that azide **6′** will slowly convert into azide **6** through a [3,3] sigmatropic rearrangement. It is important to note that product **6** can be converted by reduction into a β-amino acid derivative (Scheme 8).



Scheme 8. Synthesis of β-azido esters.

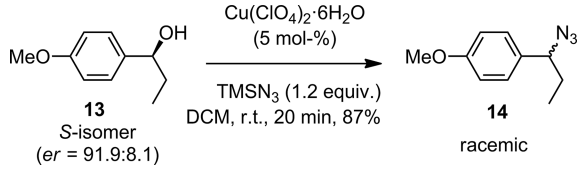
The inert nature of benzyl alcohol towards azidation under the present reaction conditions provided an opportunity to investigate the chemoselective azidation of allylic alcohols in the presence of a benzyl alcohol moiety (Scheme 9, a). Thus, (*E*)-3-[4-(hydroxymethyl)phenyl]prop-2-en-1-ol (**7**) that contains benzylic and allylic hydroxy groups in the same molecule was subjected to the present reaction conditions.



Scheme 9. Chemoselectivity study. [a] Reagents and conditions: **7**, **9**, **10**, or **12** (0.5 mmol), $TMSN_3$ (0.6 mmol), $Cu(ClO_4)_2·6H_2O$ (0.025 mmol), and dichloromethane (2 mL) at room temp. for 5–10 min.

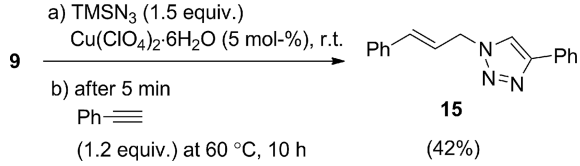
As expected, the allylic alcohol functionality underwent a selective transformation into the azide, whereas the hydroxylbenzyl group remained intact to furnish azido alcohol (*E*)-[4-(3-azidoprop-1-en-1-yl)phenyl]methanol (**8**) in 72% yield (Scheme 9, a). As expected cinnamyl alcohol (**9**) under the optimal reaction conditions furnished (*E*)-(3-azidoprop-1-en-1-yl)benzene (**11**) in 96% yield (Scheme 9, b). Interestingly, the reaction of 1-phenylprop-2-en-1-ol (**10**), which is a allylic alcohol, under the optimal conditions led to the formation of the terminal azide (*E*)-(3-azidoprop-1-en-1-yl)benzene (**11**) as the sole product in 72% yield (Scheme 9, b). Under similar reaction conditions, (*Z*)-cinnamyl alcohol (**12**) furnished (*E*)-cinnamyl azide (**11**) in 92% yield (Scheme 9, c). The results of this reaction suggest a strong possibility of a carbocation as an intermediate.

To confirm the presence of a carbocation intermediate in this transformation, chiral alcohol (*S*)-1-(4-methoxyphenyl)propan-1-ol (**13**)[37a] was subjected to the optimal reaction conditions. As expected, azide **14** was formed in 87% yield as a racemic mixture (Scheme 10). Because this reaction is led to a racemized product, it is clear beyond a doubt that the reaction proceeds through the corresponding carbocation.



Scheme 10. Azidation of chiral alcohol **13** (*er* = enantiomeric ratio).

Thereafter, this new azidation reaction, which is catalyzed by $Cu(ClO_4)_2·6H_2O$, was used in situ along with a subsequent click reaction by adding phenyl acetylene. Alcohol **9** was treated under the present reaction conditions followed by the addition of phenyl acetylene to yield the corresponding triazole **15** in 42% yield (Scheme 11).

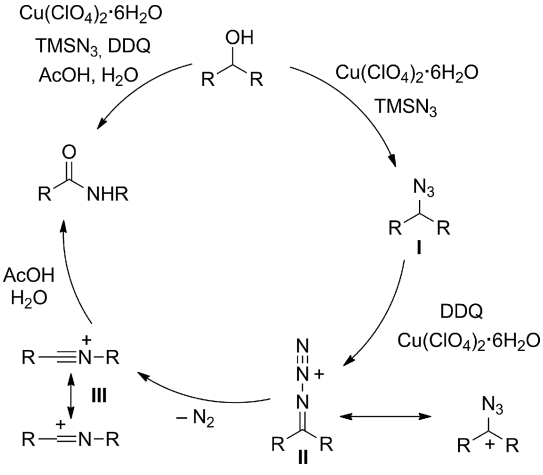


Scheme 11. One-pot click reaction.

Reaction Mechanism

We believe that the regioselectivity of the reaction is determined by the nature of the substituent that is present on the aromatic ring. The fact that the unsymmetrically substituted alcohol preferentially furnishes the azide that is benzylic to an electron-rich phenyl ring over an electron-poor one suggests that the formation of the azide is the determining factor for the observed regioselectivity. This selectivity is influenced by the formation of a stable carbocation. Azide **I** is further oxidized to give unstable azidonium intermediate **II** followed by the migration of one of the groups and the loss of nitrogen to generate nitrilium ion **III**. It was also observed that an aryl group migration is preferable over that of a vinyl group, which might be from the stabilization of azidonium intermediate **II** by a phenonium ion. Therefore, the overall observed migratory aptitude is: aryl group > vinyl group.[37b,37c]

On the basis of our work in the formation of nitriles[32a] and tetrazoles[32b] from their corresponding alcohols, a tentative mechanism has been proposed in which $Cu(ClO_4)_2{\cdot}6H_2O$ is initially treated with the alcohol and $TMSN_3$ to generate azide **I**. In the presence of DDQ, azide **I** is oxidized to give nitrilium intermediate **III**, which is trapped by water to furnish the corresponding amide (Scheme 12). The exact role of AcOH in the formation of amide product is not clear.



Scheme 12. Tentative mechanism.

Conclusions

We have reported a mild and convenient method to access amides by starting from secondary alcohols in the presence of $TMSN_3$, $Cu(ClO_4)_2{\cdot}6H_2O$, and DDQ in a one-pot reaction at ambient temperature. A detailed study was carried out to understand the effect that various substituents on the aromatic ring of an allylic alcohol would have on the regioselectivity of the reaction. This methodology has also been applied to the synthesis of azides directly from the corresponding alcohols. One of the salient features of this method is that it exhibits excellent chemoselectivity in the synthesis of ω-halo azides, which are difficult to access by conventional methods. In addition, this method offers excellent chemoselectivity in the azidation of an allylic alcohol in the presence of a benzylic alcohol moiety. Furthermore, it has been shown that this strategy provides an opportunity to synthesize (*E*)-methyl 2-(azidomethyl)-3-phenylacrylate, which can serve as a precursor in the synthesis of a β-amino acid.

Experimental Section

Typical Experimental Procedure for the Synthesis of Amides from Alcohols: $TMSN_3$ (0.08 mL, 0.6 mmol, 1.2 equiv.) was added to a well-stirred solution of alcohol **1a** (105.1 mg, 0.5 mmol, 1 equiv.), $Cu(ClO_4)_2{\cdot}6H_2O$ (9.3 mg, 0.025 mmol, 5 mol-%), and H_2O (27 mg, 1.5 mmol, 3 equiv.) in AcOH (2 mL). After 15 min, DDQ was added (136.2 mg, 0.6 mmol, 1.2 equiv.), and the mixture was stirred at room temperature until the reaction reached completion (monitored by TLC, approximately 60 min.). The reaction mixture was diluted with EtOAc, and Na_2CO_3 was added. The mixture was then passed through alumina, and the filtrate was concentrated. The residue was purified by column chromatography on silica gel.

Typical Experimental Procedure for the Synthesis of Azides from Alcohols: $TMSN_3$ (0.08 mL, 0.6 mmol, 1.2 equiv.) was added to a well-stirred solution of alcohol **3a** (89.6 mg, 0.5 mmol, 1 equiv.) and $Cu(ClO_4)_2{\cdot}6H_2O$ (9.3 mg, 0.025 mmol, 5 mol-%) in CH_2Cl_2 (2 mL). The mixture was stirred at room temperature until the reaction reached completion (monitored by TLC, approximately 15 min.). The mixture was extracted with EtOAc or DCM (3× 15 mL), and the combined organic extracts were washed with water, dried with anhydrous Na_2SO_4, and concentrated. The crude product was purified by silica gel column chromatography.

(*E*)-*N*-Phenylcinnamamide (2a):[30] White solid (103.8 mg, 93% yield); R_f = 0.4 (25% EtOAc/hexane), m.p. 149–151 °C; ref.[38] m.p. 151–153 °C. IR (KBr): ṽ = 3274, 3058, 1662, 1626, 1596, 1545, 1493, 1443, 1351, 1250, 1189, 977 cm^{-1}. ^1H NMR (400 MHz, [D_6]DMSO): δ = 10.22 (s, 1 H), 7.70 (d, J = 8.0 Hz, 2 H), 7.63–7.57 (m, 3 H), 7.47–7.39 (m, 3 H), 7.35–7.31 (m, 2 H), 7.07 (t, J = 7.2 Hz, 1 H), 6.84 (d, J = 16 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, [D_6]DMSO): δ = 163.5, 140.2, 139.3, 134.7, 129.8, 129.0, 128.8, 127.7, 123.4, 122.3, 119.2 ppm. HRMS (ESI): calcd. for $C_{15}H_{13}NNaO$ [M + Na]$^+$ 246.0895; found 246.0890.

(*E*)-*N*,3-Bis(4-methoxyphenyl)acrylamide (2b):[39] White solid (79.3 mg, 56% yield); R_f = 0.4 (25% EtOAc/hexane). IR (KBr): ṽ = 3275, 2841, 1653, 1616, 1604, 1507, 1300, 1243, 1168, 1029, 1004, 823 cm^{-1}. ^1H NMR (400 MHz, [D_6]DMSO): δ = 10.00 (s, 1 H), 7.60 (d, J = 8.4 Hz, 2 H), 7.56 (d, J = 8.4 Hz, 2 H), 7.50 (d, J = 16 Hz, 1 H), 7.00 (d, J = 8.4 Hz, 2 H), 6.90 (d, J = 8.8 Hz, 2 H), 6.65 (d, J = 16 Hz, 1 H), 3.79 (s, 3 H), 3.73 (s, 3 H) ppm. ^{13}C NMR (100 MHz, [D_6]DMSO): δ = 163.4, 160.5, 155.2, 139.4, 132.6, 129.3, 127.4, 120.6, 119.8, 114.5, 113.9, 55.3, 55.2 ppm. HRMS (ESI): calcd. for $C_{17}H_{17}NNaO_3$ [M + Na]$^+$ 306.1106; found 306.1109.

(*E*)-*N*,3-Bis(4-bromophenyl)acrylamide (2c):[10c] White solid (167.7 mg, 88% yield); R_f = 0.7 (25% EtOAc/hexane), m.p. 215–217 °C. IR (KBr): ṽ = 3285, 3048, 1652, 1619, 1589, 1530, 1486, 1396, 1335, 1245, 1183, 1070, 1007, 966, 815 cm^{-1}. ^1H NMR (400 MHz, [D_6]DMSO): δ = 10.36 (s, 1 H), 7.68–7.64 (m, 4 H), 7.59–7.51 (m, 5 H), 6.82 (d, J = 16 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, [D_6]DMSO): δ = 163.4, 139.2, 138.5, 133.9, 132.0, 131.6, 129.6, 123.0, 122.8, 121.1, 115.0 ppm. HRMS (ESI): calcd. for $C_{15}H_{12}Br_2NO$ [M + H]$^+$ 379.9286; found 379.9285.

(*E*)-*N*,3-Bis(4-chlorophenyl)acrylamide (2d):[30] White solid (105.2 mg, 72% yield); R_f = 0.4 (25% EtOAc/hexane), m.p. 207–209 °C; ref.[40] m.p. 207 °C. IR (KBr): ṽ = 3279, 3109, 3038, 1654, 1621, 1592, 1533, 1489, 1398, 1336, 1245, 1184, 1095, 1011, 969, 819 cm^{-1}. ^1H NMR (400 MHz, [D_6]DMSO): δ = 10.36 (s, 1 H), 7.72 (d, J = 8.8 Hz, 2 H), 7.64 (d, J = 8.4 Hz, 2 H), 7.59 (d, J = 16 Hz, 1 H), 7.49 (d, J = 8.4 Hz, 2 H), 7.38 (d, J = 8.8 Hz, 2 H), 6.80 (d, J = 16 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, [D_6]DMSO): δ = 163.4, 139.1, 138.1, 134.3, 133.6, 129.4, 129.0, 128.7, 127.0, 122.8, 120.8 ppm. HRMS (ESI): calcd. for $C_{15}H_{11}Cl_2NNaO$ [M + Na]$^+$ 314.0115; found 314.0117.

(*E*)-*N*,3-Bis(4-fluorophenyl)acrylamide (2e):[10c] White solid (118.0 mg, 91% yield); R_f = 0.4 (25% EtOAc/hexane), m.p. 156–158 °C. IR (KBr): ṽ = 3295, 1654, 1622, 1602, 1534, 1506, 1407, 1340, 1239, 1214, 1183, 970, 830 cm^{-1}. ^1H NMR (400 MHz, [D_6]DMSO): δ = 10.25 (s, 1 H), 7.73–7.67 (m, 4 H), 7.59 (d, J = 16 Hz, 1 H), 7.31–7.26 (m, 2 H), 7.20–7.15 (m, 2 H), 6.74 (d, J = 16 Hz,

1 H) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 162.8 (d, J = 247 Hz), 163.3, 158.0 (d, J = 238 Hz), 139.0, 135.6 (d, J = 3 Hz), 131.3 (d, J = 3 Hz), 129.8 (d, J = 9 Hz), 122.0, 120.9 (d, J = 7 Hz), 116.0 (d, J = 21 Hz), 115.3 (d, J = 22 Hz) ppm. ^{19}F NMR (376 MHz, [D$_6$]DMSO): δ = –110.9, –118.9 ppm. HRMS (ESI): calcd. for $C_{15}H_{11}F_2NNaO$ [M + Na]$^+$ 282.0706; found 282.0707.

(*E*)-*N*,3-Di-*p*-tolylacrylamide (2f):[30] White solid (90.5 mg, 72% yield); R_f = 0.4 (25% EtOAc/hexane), m.p. 172–174 °C; ref.[10b] m.p. 173–175 °C. IR (KBr): $\tilde{\nu}$ = 3307, 2916, 1656, 1624, 1521, 1405, 1337, 1241, 1171, 977, 815, 788 cm^{-1}. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 10.10 (s, 1 H), 7.60–7.50 (m, 5 H), 7.24 (d, J = 8 Hz, 2 H), 7.13 (d, J = 8 Hz, 2 H), 6.77 (d, J = 16 Hz, 1 H), 2.33 (s, 3 H), 2.26 (s, 3 H) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 163.5, 139.9, 139.6, 136.9, 132.3, 132.1, 129.7, 129.2, 127.7, 121.3, 119.2, 21.0, 20.5 ppm. HRMS (ESI): calcd. for $C_{17}H_{17}NNaO$ [M + Na]$^+$ 274.1208; found 274.1204.

(*E*)-*N*,3-Bis(2-bromophenyl)acrylamide (2g): White solid (135.3 mg 71% yield); R_f = 0.4 (25% EtOAc/hexane), m.p. 184–186 °C. IR (KBr): $\tilde{\nu}$ = 3262, 3051, 1655, 1624, 1536, 1437, 1337, 1283, 1186, 1026, 965, 742 cm^{-1}. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 9.75 (s, 1 H), 7.86 (d, J = 15.6 Hz, 1 H), 7.81–7.78 (m, 2 H), 7.74–7.68 (m, 2 H), 7.51–7.47 (m, 1 H), 7.43–7.34 (m, 2 H), 7.18–7.14 (m, 1 H), 7.08 (d, J = 15.6 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 163.4, 138.6, 136.1, 134.2, 133.3, 132.8, 131.6, 128.4, 128.1, 127.9, 127.1, 126.7, 124.9, 124.5, 117.3 ppm. HRMS (ESI): calcd. for $C_{15}H_{11}Br_2NNaO$ [M + Na]$^+$ 401.9105; found 401.9107.

(*E*)-*N*,3-Bis(2-fluorophenyl)acrylamide (2h): White solid (111.5 mg, 86% yield); R_f = 0.4 (25% EtOAc/hexane), m.p. 141–143 °C. IR (KBr): $\tilde{\nu}$ = 3288, 3059, 1662, 1630, 1543, 1483, 1457, 1341, 1228, 1105, 973, 756 cm^{-1}. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 10.10 (s, 1 H), 8.06 (m, 1 H), 7.73–7.64 (m, 2 H), 7.47–7.41 (m, 1 H), 7.29–7.25 (m, 3 H), 7.17–7.14 (m, 3 H) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 163.8, 160.6 (d, J = 250 Hz), 153.5 (d, J = 243 Hz), 133.1, 131.8 (d, J = 9.3 Hz), 129.4, 126.3 (d, J = 11 Hz), 125.4 (d, J = 8 Hz), 125.1 (d, J = 3.1 Hz), 124.6 (d, J = 4.7 Hz), 124.5 (d, J = 3.3 Hz), 123.9, 122.4 (d, J = 11.4 Hz), 116.2 (d, J = 21 Hz), 115.5 (d, J = 19 Hz) ppm. ^{19}F NMR (376 MHz, [D$_6$]DMSO): δ = –115.6, –124.9 ppm. HRMS (ESI): calcd. for $C_{15}H_{11}F_2NNaO$ [M + Na]$^+$ 282.0706; found 282.0705.

(*E*)-*N*-Phenyl-3-(*o*-tolyl)acrylamide (2iA)[10c] **and (*E*)-*N*-(*o*-Tolyl) cinnamamide (2iB):**[10c] White solid [92.6 mg 78% yield; **2iA/2iB**, 67:33 (determined by ^{1}H NMR)]. IR (KBr): $\tilde{\nu}$ = 3265, 3028, 1657, 1622, 1542, 1451, 1348, 1253, 1198, 976 cm^{-1}. Data for **2iA**: ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 10.21 (s, 1 H), 7.83–6.73 (m, 11 H), 2.41 (s, 3 H) ppm. Data for **2iB**: ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 9.47 (s, 1 H), 8.28–6.22 (m, 11 H), 2.25 (s, 3 H) ppm. HRMS (ESI): calcd. for $C_{16}H_{15}NNaO$ [M + Na]$^+$ 260.1051; found 260.1053.

(*E*)-*N*-Phenyl-3-(*p*-tolyl)acrylamide (2jA)[10c] **and (*E*)-*N*-(*p*-Tolyl) cinnamamide (2jB):**[10c] White solid [78.3 mg, 66% yield; **2jA/2jB**, 27:73 (determined by ^{1}H NMR)]. IR (KBr): $\tilde{\nu}$ = 3285, 3033, 1656, 1625, 1598, 1528, 1498, 1442, 1335, 1247, 1181, 975 cm^{-1}. Data for **2jA**: ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 10.12 (s, 1 H), 7.71–6.77 (m, 11 H), 2.26 (s, 1 H) ppm. Data for **2jB**: ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 10.16 (s, 1 H), 7.71–6.77 (m, 11 H), 2.33 (s, 1 H) ppm. HRMS (ESI): calcd. for $C_{16}H_{16}NO$ [M + H]$^+$ 238.1232; found 238.1230.

(*E*)-3-(2-Chlorophenyl)-*N*-phenylacrylamide (2kA)[10c] **and (*E*)-*N*-(2-Chlorophenyl)cinnamamide (2kB):**[40] White solid [117.2 mg, 91% yield; **2kA/2kB**, 50:50 (determined by ^{1}H NMR)]. IR (KBr): $\tilde{\nu}$ = 3297, 3061, 1663, 1626, 1597, 1527, 1473, 1440, 1340, 1241, 1178, 976 cm^{-1}. Data for **2kA**: ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.53 (d, J = 8 Hz, 1 H), 7.82 (s, 1 H), 7.78 (d, J = 15.6 Hz, 1 H), 7.57–7.38 (m, 6 H), 7.30 (t, J = 7.6 Hz, 1 H), 7.06 (t, J = 7.6 Hz, 1 H), 6.60 (d, J = 15.6 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 163.8, 143.0, 134.7, 134.4, 130.2, 129.0, 128.9, 128.1, 127.8, 124.7, 122.7, 121.7, 120.5 ppm. Data for **2kB**: ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.12 (d, J = 15.6 Hz, 1 H), 7.97 (s, 1 H), 7.67–7.52 (m, 3 H), 7.39–7.11 (m, 6 H), 6.62 (d, J = 15.6 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 163.5, 138.2, 137.9, 134.9, 132.9, 130.7, 130.2, 129.0, 127.6, 126.9, 124.5, 123.8, 120.0 ppm. HRMS (ESI): calcd. for $C_{15}H_{12}ClNNaO$ [M + Na]$^+$ 280.0505; found 280.0502.

(*E*)-3-(3-Chlorophenyl)-*N*-phenylacrylamide (2lA)[41a] **and (*E*)-*N*-(3-Chlorophenyl)cinnamamide (2lB):**[41b] White solid [101.8 mg, 79% yield; **2lA/2lB**, 35:65 (determined by ^{1}H NMR)]. IR (KBr): $\tilde{\nu}$ = 3262, 3058, 1654, 1618, 1594, 1542, 1420, 1341, 1235, 1248, 1185, 979 cm^{-1}. Data for **2lA**: ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 10.23 (s, 1 H), 7.96–7.50 (m, 11 H), 6.90 (d, J = 16 Hz, 1 H) ppm. Data for **2lB**: ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 10.41 (s, 1 H), 7.96–7.50 (m, 11 H), 6.82 (d, J = 16 Hz, 1 H) ppm. HRMS (ESI): calcd. for $C_{15}H_{12}ClNNaO$ [M + Na]$^+$ 280.0505; found 280.0506.

(*E*)-3-(4-Chlorophenyl)-*N*-phenylacrylamide (2mA)[10c] **and (*E*)-*N*-(4-Chlorophenyl)cinnamamide (2mB):**[10c] White solid [117.4 mg, 91% yield; **2mA/2mB**, 50:50 (determined by ^{1}H NMR)]. IR (KBr): $\tilde{\nu}$ = 3274, 3058, 1662, 1626, 1596, 1545, 1493, 1443, 1351, 1250, 1189, 977 cm^{-1}. Data for **2mA**: ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 10.22 (s, 1 H), 7.75–6.80 (m, 11 H) ppm. Data for **2mB**: ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 10.35 (s, 1 H), 7.75–6.80 (m, 11 H) ppm. HRMS (ESI): calcd. for $C_{15}H_{12}ClNNaO$ [M + Na]$^+$ 280.0505; found 280.0505.

(*E*)-3-(3-Bromophenyl)-*N*-phenylacrylamide (2nA)[10b] **and (*E*)-*N*-(3-Bromophenyl)cinnamamide (2nB):**[10b] Gummy white liquid [137.4 mg, 91% yield; **2nA/2nB**, 33:67 (determined by ^{1}H NMR)]. IR (KBr): $\tilde{\nu}$ = 3356, 2619, 1638, 1398, 1240, 1026, 648 cm^{-1}. Data for **2nA**: ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 10.23 (s, 1 H), 7.83 (s, 1 H), 7.70–7.25 (m, 8 H), 7.07 (t, J = 8 Hz, 1 H), 6.88 (d, J = 16 Hz, 1 H) ppm. Data for **2nB**: ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 10.40 (s, 1 H), 8.08 (s, 1 H), 7.70–7.25 (m, 9 H), 6.80 (d, J = 16 Hz, 1 H) ppm. HRMS (ESI): calcd. for $C_{15}H_{12}BrNNaO$ [M + Na]$^+$ 324.0000; found 324.0002.

(*E*)-3-(4-Fluorophenyl)-*N*-phenylacrylamide (2oA)[10c] **and (*E*)-*N*-(4-Fluorophenyl)cinnamamide (2oB):**[10b] White solid [97.7 mg, 81% yield; **2oA/2oB**, approximately 50:50 (determined by ^{1}H and ^{19}F NMR)]. IR (KBr): $\tilde{\nu}$ = 3326, 3056, 1659, 1628, 1600, 1531, 1508, 1442, 1338, 1234, 1176, 970 cm^{-1}. Data for **2oA**: ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 10.18 (s, 1 H), 7.74–6.76 (m, 11 H) ppm. Data for **2oB**: ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 10.26 (s, 1 H), 7.74–6.76 (m, 11 H) ppm. ^{19}F NMR (376 MHz, [D$_6$]DMSO): δ = –111.0, –119.1 ppm. HRMS (ESI): calcd. for $C_{15}H_{12}FNNaO$ [M + Na]$^+$ 264.0801; found 264.0800.

(*E*)-3-(4-Nitrophenyl)-*N*-phenylacrylamide (2pA)[42] **and (*E*)-*N*-(4-Nitrophenyl)cinnamamide (2pB):**[42] Yellow solid [112.7 mg, 84% yield; **2pA/2pB**, 75:25 (determined by ^{1}H NMR)]. IR (KBr): $\tilde{\nu}$ = 3365, 1693, 1630, 1597, 1542, 1500, 1448, 1327, 1298, 1255, 1160, 1109, 992, 977 cm^{-1} cm^{-1}. Data for **2pA**: ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 10.63 (s, 1 H), 8.28–6.93 (m, 10 H), 6.86 (d, J = 16 Hz, 1 H) ppm. Data for **2pB**: ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 10.30 (s, 1 H), 8.28–6.93 (m, 10 H), 6.24 (d, J = 16 Hz, 1 H) ppm. HRMS (ESI): calcd. for $C_{15}H_{12}N_2NaO_3$ [M + Na]$^+$ 291.0746; found 291.0748.

(*E*)-3-(4-Cyanophenyl)-*N*-phenylacrylamide (2qA) and (*E*)-*N*-(4-Cyanophenyl)cinnamamide (2qB): White solid [55.9 mg, 45% yield;

2qA/2qB, 88:12 (determined by ^{1}H NMR)]. IR (KBr): $\tilde{\nu}$ = 3349, 3058, 2227, 1672, 1630, 1594, 1527, 1509, 1448, 1340, 1254, 1174, 976 cm^{-1}. Data for **2qA**: ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 10.63 (s, 1 H), 7.89–6.20 (m, 11 H) ppm. Data for **2qB**: ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 10.30 (s, 1 H), 7.89–6.20 (m, 11 H) ppm. HRMS (ESI): calcd. for $C_{16}H_{12}N_2NaO$ [M + Na]$^+$ 271.0847; found 271.0853.

(*E*)-3-(Naphthalen-1-yl)-*N*-phenylacrylamide (2rA)[43a] **and (*E*)-*N*-(Naphthalen-1-yl)cinnamamide (2rB):**[43b] White solid [99.8 mg, 73% yield; **2rA/2rB**, 50:50 (determined by ^{1}H NMR)]. IR (KBr): $\tilde{\nu}$ = 3285, 3061, 1654, 1621, 1598, 1527, 1500, 1443, 1349, 1248, 1189, 971 cm^{-1}. Data for **2rA**: ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 10.16 (s, 1 H), 8.35–6.91 (m, 14 H) ppm. Data for **2rB**: ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 10.31 (s, 1 H), 8.35–6.91 (m, 14 H) ppm. HRMS (ESI): calcd. for $C_{19}H_{15}NNaO$ [M + Na]$^+$ 296.1051; found 296.1049.

(*E*)-3-(Naphthalen-2-yl)-*N*-phenylacrylamide (2sA) and (*E*)-*N*-(Naphthalen-2-yl)cinnamamide (2sB):[44] White solid [123.0 mg, 90% yield; **2sA/2sB**, 27:73 (determined by ^{1}H NMR)]. IR (KBr): $\tilde{\nu}$ = 3455, 3057, 1627, 1525, 1438, 1328, 1254, 1169, 971 cm^{-1}. Data for **2sA**: ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 10.43 (s, 1 H), 8.44 (s, 1 H), 7.99–7.06 (m, 12 H), 6.92 (d, J = 15.6 Hz) ppm. Data for **2sB**: ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 10.26 (s, 1 H), 8.14 (s, 1 H), 7.99–7.06 (m, 12 H), 6.98 (d, J = 16 Hz, 1 H) ppm. HRMS (ESI): calcd. for $C_{19}H_{15}NNaO$ [M + Na]$^+$ 296.1051; found 296.1053.

4-Methoxy-*N*-(4-methoxyphenyl)benzamide (2t):[30] White solid (100.3 mg, 78% yield); R_f = 0.3 (25% EtOAc/hexane), m.p. 200–202 °C; ref.[45] m.p. 201–202 °C. IR (KBr): $\tilde{\nu}$ = 3332, 2954, 1644, 1607, 1515, 1414, 1301, 1246, 1230, 1177, 1030, 823, 763, 666 cm^{-1}. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 9.97 (s, 1 H), 7.95 (d, J = 8 Hz, 2 H), 7.66 (d, J = 8 Hz, 2 H), 7.05 (d, J = 8 Hz, 2 H), 6.91 (d, J = 8 Hz, 2 H), 3.83 (s, 3 H), 3.74 (s, 3 H) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 164.5, 161.7, 155.4, 132.4, 129.4, 127.1, 122.0, 113.7, 113.5, 55.4, 55.1 ppm. HRMS (ESI): calcd. for $C_{15}H_{15}NNaO_3$ [M + Na]$^+$ 280.0950; found 280.0949.

(*E*)-1-(3-Azidoprop-1-en-1-yl)-4-nitrobenzene (4a):[46] Yellow gummy liquid (80.7 mg, 79% yield); R_f = 0.8 (10% EtOAc/hexane). IR (neat): $\tilde{\nu}$ = 2104 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.20 (d, J = 8.8 Hz, 2 H), 7.54 (d, J = 8.8 Hz, 2 H), 6.73 (d, J = 16 Hz, 1 H), 6.41 (dt, J = 16, 6 Hz, 1 H), 4.03 (d, J = 6 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 147.3, 142.4, 131.7, 127.5, 127.2, 124.0, 52.5 ppm. HRMS (ESI): calcd. for $C_9H_8N_4O_2$ [M]$^+$ 204.0647; found 204.0641.

(*E*)-1-(3-Azidoprop-1-en-1-yl)-4-(trifluoromethyl)benzene (4b):[47] Colorless liquid (92.0 mg, 81% yield); R_f = 0.8 (10% EtOAc/hexane). IR (neat): $\tilde{\nu}$ = 2103 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.59 (d, J = 8 Hz, 2 H), 7.49 (d, J = 8 Hz, 2 H), 6.68 (d, J = 16 Hz, 1 H), 6.33 (dt, J = 16, 6.4 Hz, 1 H), 3.99 (d, J = 6.4 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 139.4, 132.7, 129.9 (q, J = 33 Hz), 126.8, 125.6 (q, J = 4 Hz), 125.2, 124.0 (q, J = 270 Hz), 52.7 ppm. ^{19}F NMR (376 MHz, CDCl$_3$): δ = –62.6 ppm. MS: m/z = 228 [M + H]$^+$.

(*E*)-1-(3-Azidoprop-1-en-1-yl)-4-chlorobenzene (4c):[48] Colorless liquid (69.7 mg, 72% yield); R_f = 0.8 (10% EtOAc/hexane). IR (neat): $\tilde{\nu}$ = 2098 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.34–7.28 (m, 4 H), 6.60 (d, J = 15.6 Hz, 1 H), 6.21 (dd, J = 16, 6.4 Hz, 1 H), 3.94 (d, J = 6.4 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 134.5, 133.8, 133.1, 128.8, 127.8, 123.1, 52.8 ppm. HRMS: calcd. for C_9H_8Cl [M – N$_3$]$^+$ 151.0315; found 151.0313.

(*E*)-4,4′-(3-Azidoprop-1-ene-1,3-diyl)bis(chlorobenzene) (4d): Colorless liquid (136.9 mg, 90% yield); R_f = 0.8 (10% EtOAc/hexane). IR (neat): $\tilde{\nu}$ = 2099 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.37–7.28 (m, 8 H), 6.65 (d, J = 16 Hz, 1 H), 6.20 (dd, J = 16, 7.2 Hz, 1 H), 5.18 (d, J = 7.2 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 136.8, 134.2, 134.1, 134.0, 132.0, 129.0, 128.8, 128.4, 127.9, 127.0, 66.4 ppm. MS: m/z = 303. HRMS: calcd. for $C_{15}H_{11}Cl_2$ [M – N$_3$]$^+$ 261.0238; found 261.0235.

(*E*)-4,4′-(3-Azidoprop-1-ene-1,3-diyl)bis(fluorobenzene) (4e): Colorless liquid (113.9 mg, 84% yield); R_f = 0.6 (10% EtOAc/hexane). IR (neat): $\tilde{\nu}$ = 2100 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.39–7.32 (m, 4 H), 7.10–7.00 (m, 4 H), 6.66 (d, J = 16 Hz, 1 H), 6.17 (dd, J = 16, 7.2 Hz, 1 H), 5.18 (d, J = 7.2 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 162.7 (d, J = 246 Hz), 162.5 (d, J = 246 Hz), 134.3, 131.9, 128.6 (d, J = 45 Hz), 128.5 (d, J = 45 Hz), 126.4, 115.8 (d, J = 11 Hz), 115.6 (d, J = 11 Hz), 66.4 ppm. ^{19}F NMR (376 MHz, CDCl$_3$): δ = –113.1, –113.6 ppm. MS: m/z = 229 [M – N$_3$]$^+$. HRMS: calcd. for $C_{15}H_{12}F_2N$ [M – N$_2$ + H]$^+$ 244.0938; found 244.0939.

(*E*)-4,4′-(3-Azidoprop-1-ene-1,3-diyl)bis(methylbenzene) (4f): Colorless liquid (111.9 mg, 85% yield); R_f = 0.8 (10% EtOAc/hexane). IR (neat): $\tilde{\nu}$ = 2098 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.30–7.11 (m, 8 H), 6.66 (d, J = 15.6 Hz, 1 H), 6.23 (dd, J = 15.6, 7.2 Hz, 1 H), 5.15 (d, J = 7.2 Hz, 1 H), 2.35 (s, 3 H), 2.33 (s, 3 H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 138.1, 138.0, 135.6, 133.2, 132.6, 129.4, 129.3, 127.0, 126.6, 126.0, 67.1, 21.2, 21.1 ppm. MS: m/z = 221 [M – N$_3$]$^+$. HRMS: calcd. for $C_{17}H_{17}$ [M – N$_3$]$^+$ 221.1330; found 221.1328.

(*E*)-2,2′-(3-Azidoprop-1-ene-1,3-diyl)bis(bromobenzene) (4g): Colorless liquid (176.9 mg, 90% yield); R_f = 0.7 (10% EtOAc/hexane). IR (neat): $\tilde{\nu}$ = 2101 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.60–7.46 (m, 4 H), 7.37 (t, J = 7.6 Hz, 1 H), 7.26–7.10 (m, 4 H), 6.11 (dd, J = 15.6, 6.8 Hz, 1 H), 5.73 (d, J = 6.8 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 137.5, 136.0, 133.1, 133.0, 132.4, 129.7, 129.4, 128.6, 128.4, 128.0, 127.5, 127.3, 123.9, 123.3, 65.5 ppm. MS: m/z = 351 [M – N$_3$]$^+$. HRMS and elemental analysis of this compound was unsuccessful. We believe that this is a result of the instability of this compound under the employed conditions for analysis.

(*E*)-(3-Azidobut-1-en-1-yl)benzene (4h):[36f] Colorless liquid (68.4 mg, 79% yield); R_f = 0.7 (10% EtOAc/hexane). IR (neat): $\tilde{\nu}$ = 2098 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.40 (d, J = 8 Hz, 2 H), 7.33 (t, J = 8 Hz, 2 H), 7.26 (t, J = 8 Hz, 1 H), 6.60 (d, J = 16 Hz, 1 H), 6.14 (dd, J = 16, 8 Hz, 1 H), 4.20–4.13 (m, 1 H), 1.37 (d, J = 8 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 136.0, 132.1, 128.6, 128.3, 128.0, 126.6, 59.6, 20.2 ppm. MS: m/z = 131 [M – N$_3$]$^+$.

(*E*)-1-(3-Azidobut-1-en-1-yl)-4-methoxybenzene (4i):[49] Colorless liquid (84.3 mg, 83% yield); R_f = 0.6 (10% EtOAc/hexane). IR (neat): $\tilde{\nu}$ = 2100 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.33 (d, J = 8.4 Hz, 2 H), 6.87 (d, J = 8.8 Hz, 2 H), 6.54 (d, J = 15.6 Hz, 1 H), 6.01 (dd, J = 15.6, 7.6 Hz, 1 H), 4.18–4.12 (m, 1 H), 3.81 (s, 3 H), 1.36 (d, J = 6.8 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 159.5, 131.7, 128.7, 127.8, 126.0, 114.0, 59.9, 55.3, 20.3 ppm. MS: m/z = 203 [M]$^+$.

(*E*)-1-(3-Azido-3-phenylprop-1-en-1-yl)-4-fluorobenzene (4jA) and (*E*)-1-(1-Azido-3-phenylallyl)-4-fluorobenzene (4jA′): Colorless liquid [107.6 mg, 85% yield by starting from **1o**; 103.8 mg, 82% yield by starting from **1o′**; **4jA/4jA′**, approximately 50:50 (determined by ^{1}H and ^{19}F NMR)]; R_f = 0.7 (10% EtOAc/hexane). IR (neat): $\tilde{\nu}$ = 2099 cm^{-1}. Data for mixture of **4jA** and **4jA′**: ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.41–7.24 (m, 7 H), 7.09–6.99 (m, 2 H), 6.72–6.65 (m, 1 H), 6.28–6.18 (m, 1 H), 5.18 (d, J = 8 Hz, 1 H) ppm. ^{19}F NMR

(376 MHz, $CDCl_3$): δ = –113.4, –113.7 ppm. HRMS (ESI): calcd. for $C_{15}H_{12}F$ $[M - N_3]^+$ 211.0923; found 211.0927.

(*E*)-1-(3-Azido-3-phenylprop-1-en-1-yl)-2-methylbenzene (4jB) and (*E*)-1-(1-Azido-3-phenylallyl)-2-methylbenzene (4jB′): Colorless liquid [108.3 mg, 87% yield; **4jB/4jB′**, approximately 60:40 (determined by ^1H NMR)]; R_f = 0.8 (10% EtOAc/hexane). IR (neat): $\tilde{\nu}$ = 2096 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, major isomer **4jB**): δ = 7.42–7.16 (m, 9 H), 6.93 (d, J = 15.6 Hz, 1 H), 6.16 (dd, J = 15.6 Hz, 7.2 Hz, 1 H), 5.22 (d, J = 7.6 Hz, 1 H), 2.37 (s, 3 H) ppm. ^1H NMR (400 MHz, $CDCl_3$, minor isomer **4jB′**): δ = 7.42–7.16 (m, 9 H), 6.67 (d, J = 15.6 Hz, 1 H), 6.26 (dd, J = 16.0 Hz, 6.8 Hz, 1 H), 5.39 (d, J = 6.8 Hz, 1 H), 2.38 (s, 3 H) ppm. MS: m/z = 221 $[M - N_2]^+$.

(*E*)-1-(3-Azido-3-phenylprop-1-en-1-yl)-4-nitrobenzene (4jC) and (*E*)-1-(1-Azido-3-phenylallyl)-4-nitrobenzene (4jC′): Pale yellow liquid [114.8 mg, 82% yield; **4jC/4jC′**, approximately 71:29 (determined by ^1H NMR)]; R_f = 0.6 (10% EtOAc/hexane). IR (neat): $\tilde{\nu}$ = 2101 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, major isomer **4jC**): δ = 8.18 (d, J = 8.4 Hz, 2 H), 7.57–6.76 (m, 8 H), 6.46 (dd, J = 16.0 Hz, 6.8 Hz, 1 H), 5.26 (d, J = 6.8 Hz, 1 H) ppm. ^1H NMR (400 MHz, $CDCl_3$, minor isomer **4jC′**): δ = 8.23 (d, J = 8.8 Hz, 2 H), 7.57–6.76 (m, 8 H), 6.21 (dd, J = 16.0, 8.0 Hz, 1 H), 5.32 (d, J = 8.0 Hz, 1 H) ppm. MS: m/z = 238 $[M - N_3]^+$.

(1-Azido-3-chloropropyl)benzene (4k):[35] Colorless liquid (73.4 mg, 75% yield); R_f = 0.8 (10% EtOAc/hexane). IR (neat): $\tilde{\nu}$ = 2099 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.43–7.32 (m, 5 H), 4.77–4.74 (m, 1 H), 3.68–3.62 (m, 1 H), 3.51–3.46 (m, 1 H), 2.28–2.20 (m, 1 H), 2.13–2.08 (m, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.5, 129.0, 128.6, 126.9, 63.0, 41.3, 38.9 ppm. MS: m/z = 153 $[M - N_3]^+$.

1-(3-Azido-3-phenylpropoxy)naphthalene (4l): Colorless liquid (115.3 mg, 76% yield); R_f = 0.6 (10% EtOAc/hexane). IR (neat): $\tilde{\nu}$ = 2097 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.22 (d, J = 7.2 Hz, 1 H), 7.74–7.72 (m, 1 H), 7.49–7.12 (m, 9 H), 6.93 (d, J = 8.4 Hz, 1 H), 4.36–4.27 (m, 3 H), 2.46–2.39 (m, 1 H), 2.16–2.10 (m, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.3, 145.9, 133.4, 128.7, 128.4, 128.3, 127.4, 126.4, 126.0, 125.3, 125.2, 121.7, 119.6, 117.6, 63.8, 40.9, 31.8 ppm. HRMS (ESI): calcd. for $C_{19}H_{17}N_3NaO$ $[M + Na]^+$ 326.1269; found 326.1263.

1-Azido-1,2,3,4-tetrahydronaphthalene (4m):[50] Colorless liquid (79.7 mg, 92% yield); R_f = 0.8 (10% EtOAc/hexane). IR (neat): $\tilde{\nu}$ = 2095 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.31–7.12 (m, 4 H), 4.57–4.56 (m, 1 H), 2.88–2.70 (m, 2 H), 2.02–1.97 (m, 3 H), 1.82–1.56 (m, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.3, 133.7, 129.4, 129.1, 128.1, 126.1, 59.4, 29.1, 28.7, 18.9 ppm. MS: m/z = 131 $[M - N_3]^+$.

4-(1-Azidoethyl)-1,1′-biphenyl (4n):[51] Colorless liquid (96.0 mg, 86% yield); R_f = 0.8 (10% EtOAc/hexane). IR (neat): $\tilde{\nu}$ = 2099 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.61–7.57 (m, 4 H), 7.46–7.33 (m, 5 H), 4.65 (q, J = 8 Hz, 1 H), 1.56 (d, J = 8 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.0, 140.5, 139.8, 128.8, 127.5, 127.4, 127.1, 126.8, 60.8, 21.5 ppm. MS: m/z = 223. HRMS (ESI): calcd. for $C_{14}H_{13}$ $[M - N_3]^+$ 181.1017; found 181.1015.

1-(1-Azidoethyl)-4-methoxybenzene (4o):[52] Colorless liquid (74.4 mg, 84% yield); R_f = 0.8 (10% EtOAc/hexane). IR (neat): $\tilde{\nu}$ = 2103 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.25 (d, J = 8.8 Hz, 2 H), 6.90 (d, J = 8.4 Hz, 2 H), 4.56 (q, J = 6.8 Hz, 1 H), 3.81 (s, 3 H), 1.50 (d, J = 7.2 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.4, 132.8, 127.6, 114.0, 60.6, 55.2, 21.4 ppm. MS: m/z = 177 $[M]^+$.

1-(1-Azidoethyl)-4-(benzyloxy)benzene (4p):[34] Gray liquid (111.5 mg, 88% yield); R_f = 0.6 (10% EtOAc/hexane). IR (neat): $\tilde{\nu}$ = 2102 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.44–7.37 (m, 4 H), 7.33 (d, J = 8 Hz, 1 H), 7.25 (d, J = 8 Hz, 2 H), 6.97 (d, J = 8 Hz, 2 H), 5.06 (s, 2 H), 4.56 (q, J = 8 Hz, 1 H), 1.50 (d, J = 8 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.6, 136.8, 133.1, 128.6, 128.0, 127.7, 127.5, 115.0, 70.0, 60.6, 21.4 ppm. MS: m/z = 211 $[M - N_3]^+$.

[4-(1-Azidoethyl)phenoxy](*tert*-butyl)dimethylsilane (4q): Colorless liquid (112.4 mg, 81% yield); R_f = 0.8 (10% EtOAc/hexane). IR (neat): $\tilde{\nu}$ = 2104 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.18 (d, J = 8 Hz, 2 H), 6.83 (d, J = 8 Hz, 2 H), 4.55 (q, J = 8 Hz, 1 H), 1.50 (d, J = 8 Hz, 3 H), 0.98 (s, 9 H), 0.20 (s, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.5, 133.4, 127.6, 120.2, 60.7, 25.6, 21.4, 18.2, –4.4 ppm. MS: m/z = 235 $[M - N_3]^+$. HRMS: calcd. for $C_{14}H_{23}OSi$ $[M - N_3]^+$ 235.1518; found 235.1519.

1-(1-Azido-2-bromoethyl)-4-methoxybenzene (4r):[53] Colorless liquid (67.9 mg, 53% yield); R_f = 0.8 (10% EtOAc/hexane). IR (neat): $\tilde{\nu}$ = 2099 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.25 (d, J = 8.4 Hz, 2 H), 6.93 (d, J = 8.4 Hz, 2 H), 4.72 (t, J = 6.8 Hz, 1 H), 3.82 (s, 3 H), 3.54–3.52 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.1, 129.0, 128.1, 114.4, 66.4, 55.3, 35.1 ppm. MS: m/z = 214 $[M - N_3]^+$. HRMS: calcd. for $C_9H_{10}BrO$ $[M - N_3]^+$ 212.9915; found 212.9910.

2-[2-Azido-2-(4-methoxyphenyl)ethoxy]naphthalene (4s): Colorless liquid (118.2 mg, 74% yield); R_f = 0.8 (10% EtOAc/hexane). IR (neat): $\tilde{\nu}$ = 2102 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.77–7.67 (m, 3 H), 7.42 (t, J = 7.2 Hz, 1 H), 7.34–7.32 (m, 3 H), 7.19–7.11 (m, 1 H), 7.10 (s, 1 H), 6.94 (d, J = 8.4 Hz, 2 H), 4.95 (t, J = 6 Hz, 1 H), 4.24 (d, J = 6.4 Hz, 2 H), 3.82 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.9, 156.1, 134.3, 129.6, 128.4, 128.1, 127.6, 126.7, 126.4, 123.9, 118.7, 114.3, 106.9, 71.7, 64.1, 55.3 ppm. MS (m/z): 277 $[M - N_3]^+$. HRMS: calcd. for $C_{19}H_{17}N_3NaO_2$ $[M + Na]^+$ 342.1218; found 342.1217.

2-(1-Azidoethyl)thiophene (4t): Colorless liquid (55.9 mg, 73% yield); R_f = 0.7 (10% EtOAc/hexane). IR (neat): $\tilde{\nu}$ = 2104 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.29–7.28 (m, 1 H), 7.03–6.98 (m, 2 H), 4.82 (q, J = 8 Hz, 1 H), 1.62 (d, J = 8 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.8, 126.7, 125.3, 124.9, 56.4, 21.7 ppm. MS: m/z = 111 $[M - N_3]^+$. HRMS: calcd. for C_6H_7S $[M - N_3]^+$ 111.0268; found 111.0265.

(1-Azidobut-3-enyl)benzene (4u):[54] Colorless liquid (65.0 mg, 75% yield); R_f = 0.9 (10% EtOAc/hexane). IR (neat): $\tilde{\nu}$ = 2096, 1246 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.39–7.29 (m, 5 H), 5.79–5.69 (m, 1 H), 5.15–5.08 (m, 2 H), 4.49 (t, J = 7.2 Hz, 1 H), 2.63–2.48 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.2, 133.7, 128.7, 128.3, 126.9, 118.2, 65.8, 40.5 ppm. MS: m/z = 131 $[M - N_3]^+$. HRMS (ESI): calcd. for $C_{10}H_{11}$ $[M - N_3]^+$ 131.0861; found 131.0867.

(Azidomethylene)dibenzene (4v):[34] Colorless liquid (80.6 mg, 77% yield); R_f = 0.8 (10% EtOAc/hexane). IR (neat): $\tilde{\nu}$ = 2097 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.37–7.23 (m, 10 H), 5.70 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.5, 128.7, 128.0, 127.4, 68.5 ppm. MS: m/z = 167 $[M - N_3]^+$.

4,4′-(Azidomethylene)bis(methoxybenzene) (4w):[55] Colorless liquid (113.1 mg, 84% yield); R_f = 0.5 (10% EtOAc/hexane). IR (neat): $\tilde{\nu}$ = 2096 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.21 (d, J = 8 Hz, 4 H), 6.87 (d, J = 8 Hz, 4 H), 5.63 (s, 1 H), 3.78 (s, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.2, 132.0, 128.5, 113.9, 67.6, 55.2 ppm. HRMS (ESI): calcd. for $C_{15}H_{16}NO_2$ $[M - N_2 + H]^+$ 242.1181; found 242.1180.

(3-Azidopent-1-yn-1-yl)benzene (4x): Colorless liquid (48.2 mg, 52% yield); R_f = 0.8 (10% EtOAc/hexane). IR (neat): $\tilde{\nu}$ = 2098 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.48–7.46 (m, 2 H), 7.33–7.32 (m, 3 H), 4.26 (t, J = 8 Hz, 1 H), 1.85–1.78 (m, 2 H), 1.09 (t, J = 8 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 131.9, 128.7, 128.3, 122.1, 87.1, 84.4, 54.9, 28.8, 10.1 ppm. MS: m/z = 185. HRMS (ESI): calcd. for $C_{11}H_{11}$ $[M - N_3]^+$ 143.0861; found 143.0861.

(*E*)-Methyl 2-(Azidomethyl)-3-phenylacrylate (6):[56] Colorless liquid (82.5 mg, 76% yield); R_f = 0.5 (10% EtOAc/hexane). IR (neat): $\tilde{\nu}$ = 2109 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.98 (s, 1 H), 7.44–7.39 (m, 5 H), 4.19 (s, 2 H), 3.89 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.5, 144.5, 134.1, 129.6, 129.5, 128.7, 126.6, 52.4, 47.0 ppm. HRMS (ESI): calcd. for $C_{11}H_{11}N_3NaO_2$ $[M + Na]^+$ 240.0749; found 240.0747.

(*E*)-[4-(3-Azidoprop-1-en-1-yl)phenyl]methanol (8): White solid (68.1 mg, 72% yield); R_f = 0.2 (20% EtOAc/hexane), m.p. 38–40 °C. IR (neat): $\tilde{\nu}$ = 2101 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.40–7.32 (m, 4 H), 6.64 (d, J = 16 Hz, 1 H), 6.27–6.20 (m, 1 H), 4.67 (s, 2 H), 3.94 (d, J = 6.8 Hz, 2 H), 1.87 (br. s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.8, 135.3, 134.1, 127.2, 126.8, 122.4, 64.9, 53.0 ppm. MS: m/z = 189. HRMS (ESI): calcd. for $C_{10}H_{11}O$ $[M - N_3]^+$ 147.0810; found 147.0807.

(*E*)-(3-Azidoprop-1-en-1-yl)benzene (11):[57] Colorless liquid (76.4 mg, 96% yield by starting from **9**; 57.3 mg, 72% yield by starting from **10**; 73.2 mg, 92% yield by starting from **12**); R_f = 0.8 (10% EtOAc/hexane). IR (neat): $\tilde{\nu}$ = 2100 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.41–7.25 (m, 5 H), 6.65 (d, J = 16 Hz, 1 H), 6.26–6.22 (m, 1 H), 3.94 (d, J = 8 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.0, 134.5, 128.6, 128.2, 126.6, 122.4, 53.0 ppm. MS: m/z = 159 $[M]^+$.

1-(1-Azidopropyl)-4-methoxybenzene (14):[58] Colorless liquid (83.2 mg, 87% yield); R_f = 0.8 (10% EtOAc/hexane). IR (neat): $\tilde{\nu}$ = 2095 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.22 (d, J = 8.8 Hz, 2 H), 6.90 (d, J = 8.4 Hz, 2 H), 4.29 (t, J = 7.2 Hz, 1 H), 3.81 (s, 3 H), 1.90–1.70 (m, 2 H), 0.91 (t, J = 7.6 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.4, 131.6, 128.1, 114.0, 67.4, 55.2, 29.1, 10.8 ppm. MS: m/z = 191 $[M]^+$.

1-Cinnamyl-4-phenyl-1*H*-1,2,3-triazole (15):[59] Yellow solid (54.8 mg, 42% yield); R_f = 0.1 (10% EtOAc/hexane), m.p. 133–135 °C; ref.[59] m.p. 134 °C. IR (neat): $\tilde{\nu}$ = 3030, 1670, 1449, 1224, 1074, 970 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.84–7.80 (m, 3 H), 7.43–7.38 (m, 4 H), 7.36–7.25 (m, 4 H), 6.69 (d, J = 15.6 Hz, 1 H), 6.37 (dt, J = 16, 6.8 Hz, 1 H), 5.16 (dd, J = 6.8, 1.2 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.1, 135.4, 135.3, 130.6, 128.8, 128.7, 128.5, 128.1, 126.7, 125.7, 121.9, 119.3, 52.4 ppm. HRMS (ESI): calcd. for $C_{17}H_{15}N_3Na$ $[M + Na]^+$ 284.1164; found 284.1165.

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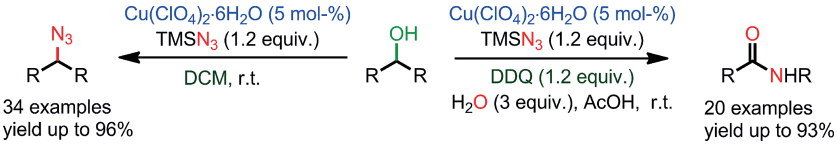

A mild and convenient method for the synthesis of amides has been explored by using secondary alcohols, $Cu(ClO_4)_2·6H_2O$ as a catalyst, and trimethylsilyl azide ($TMSN_3$) as a nitrogen source in the presence of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) at ambient temperature. This method has also been adapted to the preparation of azides directly from their corresponding alcohols.

Synthetic Methods

Keywords: Synthetic methods / Chemoselectivity / Alcohols / Azides / Amides / Copper

