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Article

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# Base-controlled Regiodivergent Azidation of Trifluoromethyl Alkenyl Triflates: Transition-Metal-Free Access to $CF_3$-Containing Allyl Azides and Alkenyl Azides

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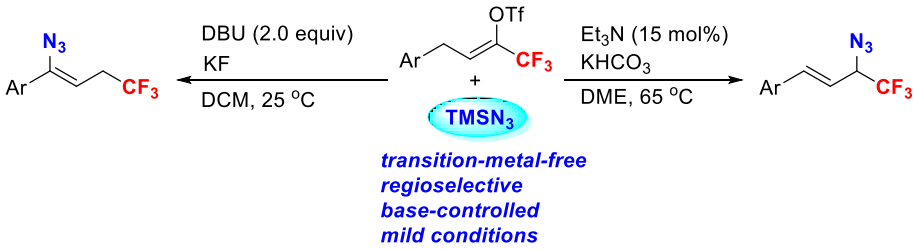



**ABSTRACT:** A base-controlled regiodivergent azidation of trifluoromethyl alkenyl triflates providing either (*E*)-3-azido-1-aryl-4,4,4-trifluorobut-1-ene ($CF_3$-containing allyl azides) or (*Z*)-1-azido-1-aryl-4,4,4-trifluorobut-1-ene ($CF_3$-containing alkenyl azides) is described. Catalyzed by $Et_3N$, the azidation of trifluoromethyl alkenyl triflates with $TMSN_3$ gave $CF_3$-containing allyl azides. On the other hand, using stoichiometric DBU, the regioisomeric azidation products, $CF_3$-containing alkenyl azides, were obtained in good yield. A further transformation for $CF_3$-containing

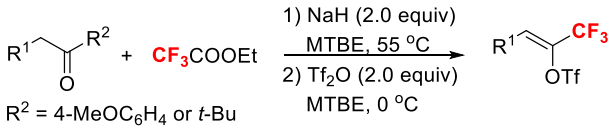
amines, triazoles, and azirines highlights the practical applicability of this transition-metal-free protocol.

## INTRODUCTION

As highly important class of nitrogen-containing compounds, organic azides have been recognized as versatile synthetic building blocks, which can be easily transformed into amines, isocyanates, heterocycles, *etc*.[1] In recent years, with the rapid development of the well-known "Click chemistry", the copper-catalyzed azide-alkyne cycloaddition reactions have enjoyed an increasing attention.[2] More importantly, many organic azides have been reported to show significant biological activities such as antiviral activity and enzyme inhibition.[3] So accordingly, it will be valuable to introduce an azide group in a mild and efficient process, especially in regioselective reaction. As we know, the introduction of trifluoromethyl group into biologically active compounds often improves their physiochemical properties such as lipophilicity, metabolic stability, activity *etc.*[4] Thus, the molecules containing both trifluoromethyl group and azide group will offer effective organic building blocks. For instance, efficient synthesis of biological molecules containing trifluoromethyl group might be hopeful by the various derivation reactions of the azide group. However, only a few methodologies for the synthesis of $CF_3$-containing organoazides have been developed. Using trifluoromethylated reagents and trimethylsilyl azide ($TMSN_3$) as the source of the $CF_3$ and azide group, Liu and co-workers reported copper-catalyzed intermolecular trifluoromethylazidation of alkenes, allenes, and

alkynes to afford $CF_3$-containing organoazides.[5] Likewise, Liang reported trifluoromethylazidation and carbocyclization of 1,6-enynes.[6] And, Hartwig and co-workers reported the $Fe(OAc)_2$-catalyzed trifluoromethylazidation of olefins in complex natural products with excellent regioselectivity.[7] With good environmental compatibility and versatility, Masson reported trifluoromethylazidation of alkenes through photo-redox catalyzed by ruthenium.[8] In addition to the above mentioned cases, avoiding the use of expensive or unstable trifluoromethylating reagents, a promising approach for the synthesis of trifluoromethyl-containing compounds is through the use of appropriate trifluoromethylated building blocks. In recent years, our group has committed to the synthesis of organic fluorides.[9] To this end, useful trifluoromethylated building blocks, trifluoromethyl alkenyl triflates (Scheme 1), were reported and successfully applied in the synthesis of a diverse range of trifluoromethyl-containing compounds.[9d,9f] Meanwhile, the idea of catalytic regioselective reaction is highly attractive for the possibility of gaining divergent products from the same reactants.[10] And the transition-metal-free reaction is more favorable owing to the strict restriction on the residual amount of heavy metals in pharmaceutical and material industry. In this context, we herein report a base-controlled regioselective azidation of trifluoromethyl alkenyl triflates with trimethylsilyl azide in the presence of organic amines, which gave $CF_3$-containing allyl azides and aryl alkenyl azides.

**Scheme 1 Synthesis of trifluoromethyl alkenyl triflates[9d]**

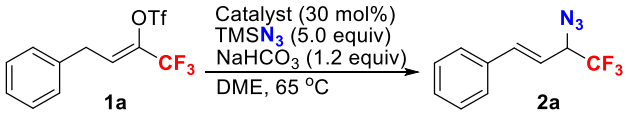



## RESULTS AND DISCUSSION

The investigation using (*Z*)-4-phenyl-1,1,1-trifluorobut-2-en-2-yl trifluoromethanesulfonate (**1a**) as the model substrate and trimethylsilyl azide as the azide source was summarized in Table 1. With $Et_3N$ (30 mol%) as catalyst, DME as solvent, it was pleasing to find that the (*E*)-3-azido-1-phenyl-4,4,4-trifluorobut-1-ene (allyl azide product **2a**) was formed in 13% yield at 65 °C for 12 h (Table 1, entry 1). To further improve this transformation, the plan of increasing the equivalent of $Et_3N$ to 1.2 equiv or introducing $NaHCO_3$ (1.2 equiv) as the additives was carried out (Table 1, entries 2 and 3). To our satisfaction, the results indicated that the azidation reaction proceeded efficiently and a higher yield (80%) of **2a** was obtained when $NaHCO_3$ was used as the additive. Under the same conditions, using $NaHCO_3$ as the additive, we also tested other various organic amines. However, the desired product (**2a**) was afforded in a lower yield (Table 1, entries 5-12). It should be noted that no azidation product was detected when pyridine was used as catalyst (Table 1, entry 4). To further improve the reaction efficiency, the influence of equivalent of $Et_3N$ on the reaction was examined (Table 1, entries 13-16). The reaction is sensitive to the amount of $Et_3N$. Slightly decreasing the catalyst loading to 15 mol% improved the efficiency of this transformation and **2a** was obtained in 84% yield. Meanwhile, at room temperature, $Et_3N$ has low catalytic activity and the yield was only 25% (Table

1, entry 17).

**Table 1 Optimization of the formation of 2a based on catalysts**[a]



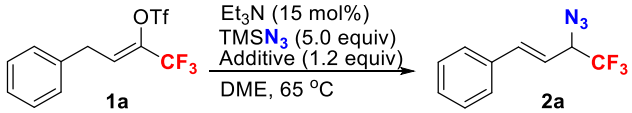

| Entry | Catalyst | Conv. **1a**/%[b] | Yield **2a**/%[b] |
|---|---|---|---|
| 1[c] | $Et_3N$ | 20 | 13 |
| 2[d] | $Et_3N$ | 100 | 78 |
| 3 | $Et_3N$ | 100 | 80 |
| 4 | Py | 0 | 0 |
| 5 | DBU | 100 | 65 |
| 6 | DBN | 100 | 70 |
| 7 | TBD | 90 | 52 |
| 8 | DABCO | 100 | 71 |
| 9 | *i*-$Pr_2NEt$ | 70 | 52 |
| 10 | DMAP | 100 | 64 |
| 11 | TMEDA | 100 | 68 |
| 12 | $[(CH_3)_3Si]_2NCH_3$ | 100 | 77 |
| 13[e] | $Et_3N$ | 100 | 83 |
| 14[f] | $Et_3N$ | 100 | 84 |
| 15[g] | $Et_3N$ | 90 | 71 |
| 16[h] | $Et_3N$ | 73 | 60 |
| 17[i] | $Et_3N$ | 43 | 25 |

[a]Reaction conditions: **1a** (0.2 mmol), $TMSN_3$ (1.0 mmol), catalyst (30 mol%), $NaHCO_3$ (0.24 mmol), DME (2 mL) at 65 °C for 12 h under Ar atmosphere. [b]The yield was determined by $^1H$ NMR with dimethyl terephthalate as an internal standard. [c]Without $NaHCO_3$. [d]$Et_3N$ 120 mol%, without $NaHCO_3$. [e]$Et_3N$ 20 mol%. [f]$Et_3N$ 15 mol%. [g]$Et_3N$ 10 mol%. [h]$Et_3N$ 5 mol%. [i]$Et_3N$ 15 mol%, 25 °C.

Concerning the role of $NaHCO_3$ in this transformation, we examined the effect of other additives including $KHCO_3$ and KF. As shown in Table 2, the yield was slightly increased to 89% when $KHCO_3$ was employed (Table 2, entry 2). The

reaction was executed under Ar atmosphere, and a slightly lower yield was obtained in air (Table 2, entry 6). The control experiment was performed in the absence of $Et_3N$ and the desired product was formed in only 22% yield (Table 2, entry 5). Remarkably, raising the amount of $KHCO_3$ to 3.0 equiv has a negative effect on this transformation (Table 2, entry 4). Further screening the optimal conditions containing solvents and the equivalent of $TMSN_3$ were also carried out (Table S1 and S2). Among the tested solvents, glycol dimethyl ether (DME) was the optimized one. To our delight, when the amount of $TMSN_3$ was decreased to 2.0 equiv, the yield of **2a** was improved to 94% (Table 2, entry 7). In addition, when $NaN_3$ was used as azide source, the yield was drastically declined (Table S2). Thus, after optimizing the reaction conditions, the reaction with 15 mol% $Et_3N$, 1.2 equiv of $KHCO_3$ and 2.0 equiv of $TMSN_3$ in DME at 65 °C for 12 h under Ar atmosphere was found to produce the highest yield of $CF_3$-containing allyl azide (**2a**).

**Table 2 Optimization of the formation of 2a based on additives**[a]




| Entry | Additive | Conv. **1a**/%[b] | Yield **2a**/%[b] |
|---|---|---|---|
| 1 | $NaHCO_3$ | 100 | 84 |
| 2 | $KHCO_3$ | 100 | 89 |
| 3 | KF | 100 | 86 |
| 4[c] | $KHCO_3$ | 100 | 80 |
| 5[d] | $KHCO_3$ | 48 | 22 |
| 6[e] | $KHCO_3$ | 100 | 85 |
| 7[f] | $KHCO_3$ | 100 | 94 |

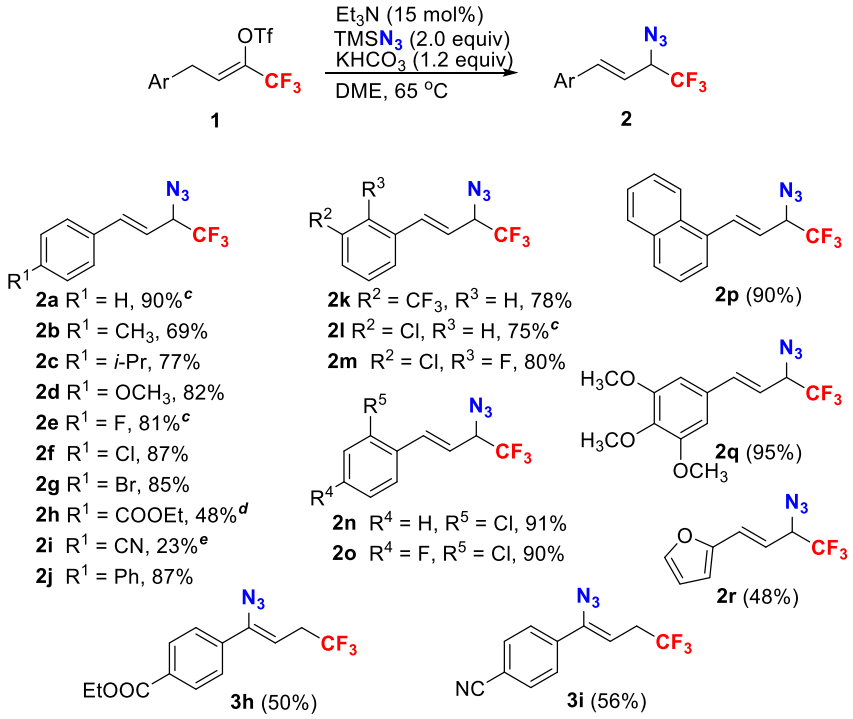
[a]Reaction conditions: **1a** (0.2 mmol), $TMSN_3$ (1.0 mmol), $Et_3N$ (15 mol%), additive (0.24 mmol), DME (2 mL) at 65 °C for 12 h under Ar atmosphere. [b]The yield was

determined by $^{1}$H NMR with dimethyl terephthalate as an internal standard. [c]$KHCO_3$ 3.0 equiv. [d]$KHCO_3$ 3.0 equiv, without $Et_3N$. [e]In air. [f]$TMSN_3$ 2.0 equiv.

With the optimal conditions in hand, the scope of the substrate was explored and displayed in Table 3. A variety of trifluoromethyl alkenyl triflates (**1**) bearing both electron-donating and electron-withdrawing substituents on the aromatic ring were smoothly transformed into the corresponding desired products (**2**) with isolated yield up to 95%. The steric and electronic effects have little impact on the reaction. Trifluoromethyl-substituted substrate (**1k**) gave the yield of 78%. Substrates bearing electron-withdrawing functional groups, such as chlorine, bromine and fluorine, in different position exhibited good yields in this transformation (**2e**, **2f**, **2g**, **2l**, and **2n**). Trifluoromethyl alkenyl triflates with di- and tri-substituted phenyl ring proved to be favorable substrates, affording the azidation products in excellent yields (**2m**, **2o** and **2q**). Reactions of biphenyl and naphthyl with $TMSN_3$ afforded the products in 87% and 90% yields, respectively (**2j** and **2p**). The heterocyclic substrate (**1r**) exhibited lower reactivity and the product (**2r**) was isolated in 48% yield. It is worth mentioning that the ethoxycarbonyl and cyano-substituted allyl azide products were obtained in lower yields (**2h** and **2i**), whereas the alkenyl azide products, (*Z)*-ethyl 4-(1-azido-4,4,4-trifluorobut-1-enyl)benzoate (**3h**) and (*Z*)-1-azido-1-(4-cyanophenyl)-4,4,4-trifluorobut-1-ene (**3i**), were isolated as side products in 50% and 56% yields, respectively. In addition, the substrate with a linear aliphatic chain, for example (*Z*)-1,1,1-trifluorotridec-2-en-2-yl

trifluoromethanesulfonate, was also tried in this process, but it was almost no reaction. A single-crystal of **2q** was prepared, and its structure was confirmed by X-ray single-crystal diffraction (Fig. S1).

**Table 3 Reaction scope for allyl azide products under optimal conditions**[a,b]

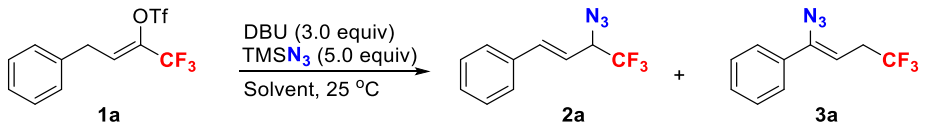



[a]Reaction conditions: **1** (0.2 mmol), $TMSN_3$ (0.4 mmol), $Et_3N$ (15 mol%), $KHCO_3$ (0.24 mmol), solvent (2 mL) at 65 °C for 12 h under Ar atmosphere. [b]Isolated yield. [c]The substrate **1** was conducted in 0.5 mmol. [d]Reaction temperature: 40 °C; 50% yield of **3h** was isolated. [e]Reaction temperature: 40 °C; 56% yield of **3i** was isolated.

As mentioned above, the substrates with ethoxycarbonyl and cyano groups (**1h** and **1i**) gave some alkenyl azide products (**3h** and **3i**) in the reaction. It is attributed to the increased acidity of 1-H in intermediate **B** (see Scheme 3) resulting from electron-withdrawing effect of ethoxycarbonyl and cyano groups, which makes the

double bond migration easier (see Scheme 3 and the discussion about the plausible reaction mechanism for details). We speculated a stronger base may also benefit the formation of alkenyl azide products. Attracted by the promise and potential of obtaining azide products with different regioselectivity, we focused on the synthesis of alkenyl azide products in the next step. Herein, the initial experiment was conducted with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 3.0 equiv), $TMSN_3$ (5.0 equiv) in $CH_2Cl_2$ solvent at room temperature. Gratifyingly, the desired alkenyl azide (**3a**) was formed in 68% yield (Table 4, entry 1). To further improve this transformation, various solvents, such as DME, THF, $PhCH_3$ and DMF *etc.*, were tested in this transformation and confirmed $CH_2Cl_2$ was the best one. However, other bases such as 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) turned out to be slightly ineffective for this transformation (Table 5, entries 2 and 3). Also, only trace amounts of the alkenyl product (**3a**) were detected when we use DABCO, DMAP, $Et_3N$ and TMEDA as base. Instead, allyl product (**2a**) was detected as byproduct (Table 5, entries 4-7).

**Table 4 Optimization of the formation of 3a based on solvents**[a]



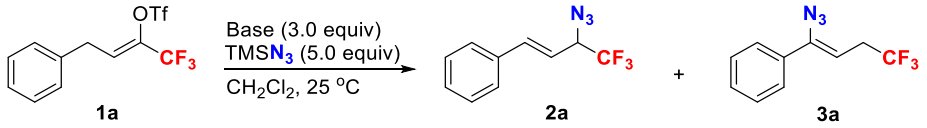

1a 2a 3a

| Entry | Solvent | Conv. **1a**/%[b] | Yield **2a**/%[b] | Yield **3a**/%[b] |
|---|---|---|---|---|
| 1 | DME | 100 | 7 | 66 |
| 2 | $Et_2O$ | 100 | 5 | 50 |
| 3 | THF | 100 | 4 | 28 |
| 4 | $CH_3CN$ | 100 | 0 | 60 |
| 5 | $PhCH_3$ | 100 | 3 | 47 |

| | | | | |
|---|---|---|---|---|
| 6 | $CH_2Cl_2$ | 100 | 0 | 68 |
| 7 | $CCl_4$ | 100 | 6 | 53 |
| 8 | $ClCH_2CH_2Cl$ | 100 | 4 | 67 |
| 9 | DMF | 100 | 9 | 14 |
| 10 | DMSO | 100 | 0 | trace |
| 11 | NMP | 100 | 15 | 31 |
| 12[c] | $CH_2Cl_2$ | 100 | 17 | 66 |
| 13[d] | $CH_2Cl_2$ | 100 | 11 | 62 |
| 14[e] | $CH_2Cl_2$ | 100 | 14 | 60 |

[a]Reaction conditions: **1a** (0.2 mmol), $TMSN_3$ (1.0 mmol) and solvent (1 mL) were stirred at room temperature. And then the base (0.6 mmol, diluted with 1 mL of solvent) was added slowly at 25 ºC for 1 h - 2 h. [b]The yield was determined by $^1H$ NMR with dimethyl terephthalate as an internal standard. [c]-40 ºC. [d]-20 ºC. [e]0 ºC.

**Table 5 Optimization of the formation of 3a based on bases[a]**



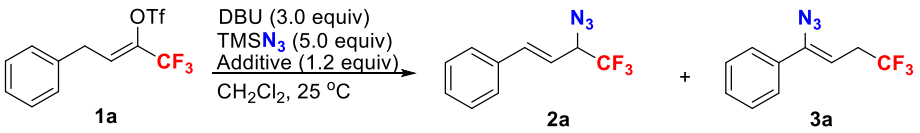

| Entry | Base | Conv. **1a**/%[b] | Yield **2a**/%[b] | Yield **3a**/%[b] |
|---|---|---|---|---|
| 1 | DBU | 100 | 0 | 68 |
| 2 | DBN | 100 | 0 | 56 |
| 3 | TBD | 100 | 0 | 66 |
| 4 | DABCO | 92 | 55 | <1 |
| 5 | DMAP | 100 | 32 | 4 |
| 6 | $Et_3N$ | 100 | 19 | 23 |
| 7 | TMEDA | 100 | 35 | 7 |

[a]Reaction conditions: **1a** (0.2 mmol), $TMSN_3$ (1.0 mmol) and $CH_2Cl_2$ (1 mL) were stirred at room temperature. And then the base (0.6 mmol, diluted with 1 mL of $CH_2Cl_2$) was added slowly at 25 °C for 1 - 2 h. [b]The yield was determined by $^1H$ NMR with dimethyl terephthalate as an internal standard.

We next explored the effect of various additives (Table 6). It was found that both

$KHCO_3$ and KF could improve the yield to some extent, and KF led to a higher yield of 72%, although trace amount of allyl azide product was detected (Table 6, entries 1 and 4). Other additives such as $K_2CO_3$, $Cs_2CO_3$, NaF and CsF were invalid for improving the yield of this transformation (Table 6, entries 2, 3 and 5, 6). Notably, the occurrence of the alkenyl azide reaction was hindered when *n*-$Bu_4N^+F^-$ was chosen as an additive (Table 6, entry 7). In addition, air atmosphere has little impact on this process (Table 6, entry 8). The equivalent of $TMSN_3$ and DBU were also tested (illustrate several examples in Table 6 and see Table S3 for details). Raising and reducing the amount of $TMSN_3$ resulted in a slight decrease of $TMSN_3$ loading has an adverse effect on improving the yield of alkenyl azide product (Table 6, entries 10 and 11). To our satisfaction, when the equivalent of DBU decreased to 2.0, the yield was further improved to 74% (Table 6, entry 9).

**Table 6 Optimization of the formation of 3a based on additives**[a]



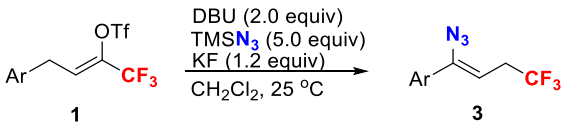

| Entry | Additive | Conv. **1a**/%[b] | Yield **2a**/%[b] | Yield **3a**/%[b] |
|---|---|---|---|---|
| 1 | $KHCO_3$ | 100 | 0 | 70 |
| 2 | $K_2CO_3$ | 100 | 0 | 64 |
| 3 | $Cs_2CO_3$ | 100 | 9 | 66 |
| 4 | KF | 100 | 8 | 72 |
| 5 | NaF | 100 | 2 | 62 |
| 6 | CsF | 100 | 4 | 64 |
| 7 | *n*-$Bu_4NF$ | 100 | 36 | 2 |
| 8[c] | KF | 100 | 11 | 71 |
| 9[d] | KF | 100 | 10 | 74 |
| 10[e] | KF | 100 | 0 | 59 |
| 11[f] | KF | 100 | 0 | 67 |

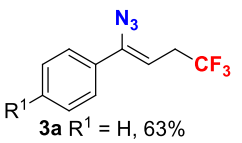
[a]Reaction conditions: **1a** (0.2 mmol), $TMSN_3$ (1.0 mmol), additive (0.24 mmol) and

$CH_2Cl_2$ (1 mL) were stirred at room temperature. And then DBU (0.6 mmol, diluted with 1 mL of $CH_2Cl_2$) was added slowly at 25 °C for 1 h - 2 h. [b]The yield was determined by $^1H$ NMR with dimethyl terephthalate as an internal standard. [c]In air. [d]DBU 2.0 equiv. [e]$TMSN_3$ 3.0 equiv. [f]$TMSN_3$ 10.0 equiv.

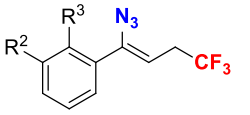
Herein, with the optimum conditions in hand, we turned our attention to the substrate scope and generality of this process. The results were summarized in Table 7. The alkenyl azidation reaction of trifluoromethyl alkenyl triflates (**1**) bearing electron-rich and electron-deficient aryl substituents proceeded smoothly to afford the corresponding products **3** in moderate to good yields. Halo substituents on the phenyl ring at different position were well tolerated (**3e**, **3f**, **3g**, **3l** and **3n**). In addition, trifluoromethyl alkenyl triflates with disubstituted phenyl were also suitable and afforded **3m** and **3o** in 67% and 61% yields. It is noteworthy that methoxy-substituted trifluoromethyl alkenyl triflates performed well under the standard conditions and gave the corresponding products in good yield as well as ethoxycarbonyl substituted substrate (**3d**, **3q** and **3h**). Moreover, both of biphenyl and naphthyl substitutes were tolerated in this process and showed almost the same efficiency (**3j** and **3p**). Cyano-substituted substrate (**1i**) also provided the desired product in moderate yield, although the unknown byproducts were detected by $^1H$ NMR analysis (**3i**). A single-crystal of **3j** was prepared, and its configuration was confirmed to be *Z* by X-ray single-crystal diffraction (Fig. S2).

**Table 7 Reaction scope for alkenyl azide products under optimal conditions**[a,b]

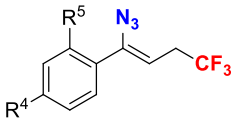


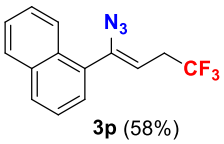

**3a** $R^1$ = H, 63%
**3b** $R^1$ = $CH_3$, 68%
**3c** $R^1$ = *i*-Pr, 67%
**3d** $R^1$ = $OCH_3$, 79%
**3e** $R^1$ = F, 58%
**3f** $R^1$ = Cl, 77%
**3g** $R^1$ = Br, 68%
**3h** $R^1$ = COOEt, 77%
**3i** $R^1$ = CN, 55%
**3j** $R^1$ = Ph, 60%



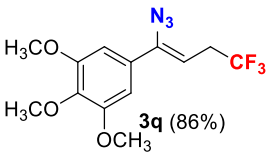

**3k** $R^2$ = $CF_3$, $R^3$ = H, 64%
**3l** $R^2$ = Cl, $R^3$ = H, 69%
**3m** $R^2$ = Cl, $R^3$ = F, 67%




**3n** $R^4$ = H, $R^5$ = Cl, 68%
**3o** $R^4$ = F, $R^5$ = Cl, 61%




**3p** (58%)

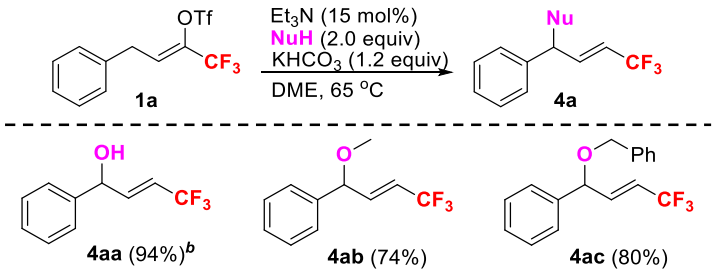



**3q** (86%)

[a]Reaction conditions: **1** (0.5 mmol), $TMSN_3$ (2.5 mmol), KF (0.6 mmol) and $CH_2Cl_2$ (2.5 mL) were stirred at room temperature. And then DBU (1.0 mmol, diluted with 2.5 mL of $CH_2Cl_2$) was added slowly at 25 °C for 1 h - 2 h. [b]Isolated yield.

To gain further insight into this transformation, using $Et_3N$ as catalyst and $KHCO_3$ as additive, other nucleophilic reagents such as $H_2O$, MeOH and $PhCH_2OH$ were investigated in DME at 65 °C (Scheme 2). The process proceeded smoothly and afforded the products in moderate to excellent yield. But the substitutional positions of nucleophilic reagents were all different from $TMSN_3$. And no **3a** was formed upon the treatment of **2a** with DBU (3 equiv), which excludes the conversion of **2** to **3**.

**Scheme 2 The scope of other nucleophilic reagents in this transformation**[a]

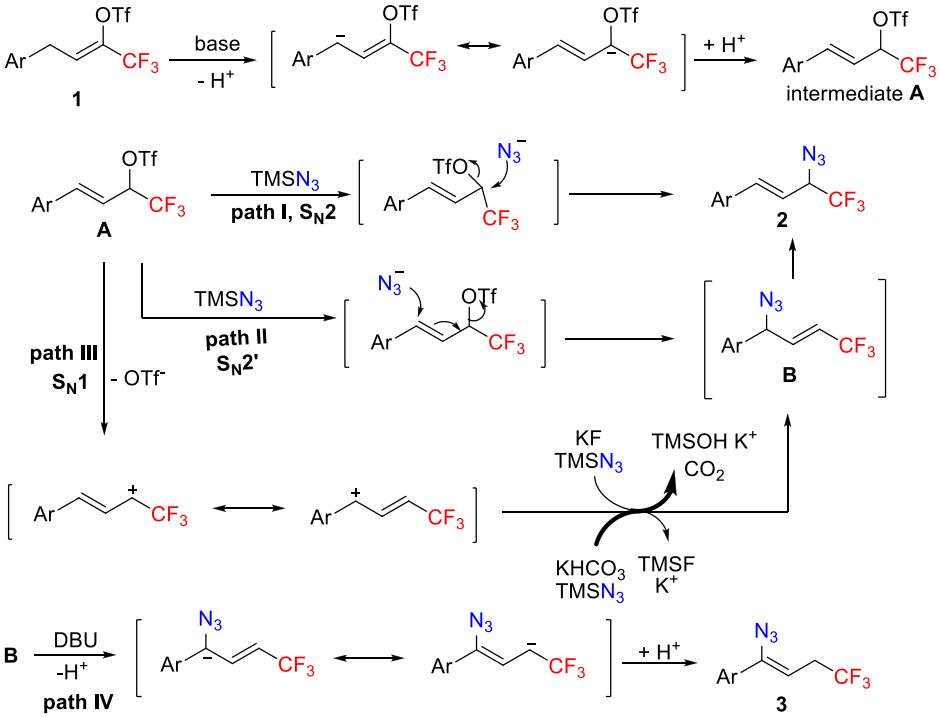



[a]Reaction conditions: **1** (0.5 mmol), NuH (1.0 mmol), $Et_3N$ (15 mol%), $KHCO_3$ (0.6 mmol), solvent (5 mL) at 65 °C for 12 h under Ar atmosphere. [b]Isolated yield.

So according to the present experimental results and previous reports, the possible mechanism for azidation of trifluoromethyl alkenyl triflates was shown in Scheme 3, although the detailed mechanism remained unclear. Initially, the double bond isomerization intermediate **A** was obtained under base conditions. And then the intermediate **A** could be transformed into allyl azide products in three possible pathways. One way was that the –OTf group was directly substituted by $TMSN_3$ via a $S_N2$ reaction to form the allyl azide products **2** (path I). The other was $S_N2'$ substitution, $N_3$ anion took a conjugate addition over the double bond, and –OTf group left to afford intermediate **B**. The intermediate **B** was difficult to be isolated and was rearranged to allyl azide products **2** quickly in $Et_3N$ catalytic condition (path II). And the third one was that the leaving of–OTf in intermediate **A** resulted in the formation of $CF_3$-allyl cations.[11] Having two resonances, the relative stable $CF_3$-allyl cations could be captured by $TMSN_3$ to afford intermediate **B**. And then, the allyl

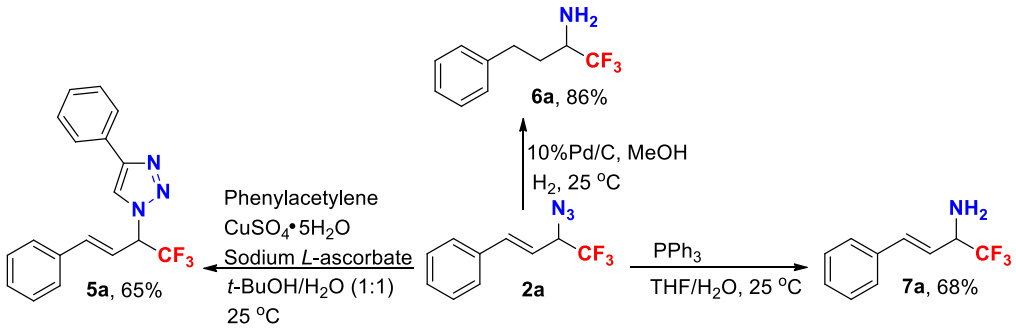
azide products **2** were formed via a quick [3,3] rearrangement of intermediate **B** in $Et_3N$ catalytic condition (path III).[12] On the other hand, the alkenyl azide products **3** could be formed from intermediate **B** after double bond migration under DBU action since the stronger alkaline DBU was beneficial for this transformation (path IV).

**Scheme 3 Plausible reaction mechanism**



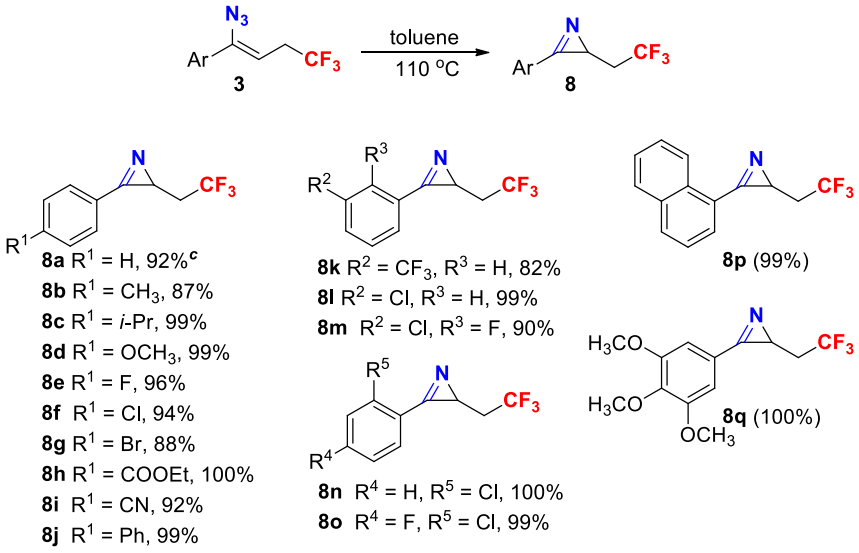

Considering the synthetic utility of these products, further transformation of the azidation products was explored. For example, as shown in Scheme 4, a click reaction of **2a** with phenylacetylene afforded the $CF_3$-containing triazoles **5a** in 65% yield. The $CF_3$-substituted amines **6a** and **7a** were obtained through the reduction of **2a** in 86% and 68% yields.

**Scheme 4 Transformations of allyl azide product 2a**




Additionally, the structures of azirines are important in functional molecules such as medicines and agricultural chemicals. And also, azirines can be used for the synthesis of various nitrogen-containing heterocycles. In recent years, the exploration of new methodologies for the efficient synthesis of $CF_3$-containing azirines is much attractive due to the trifluoromethyl and azirines are widely utilized. However, the synthesis of such unique structures was quite rare.[5c,13] Herein, the transformation of alkenyl azide products **3** into $CF_3$-containing azirines **8** is put on our schedule. As shown in Scheme 5, bearing electron-rich and electron-deficient aryl substituents, the $CF_3$-containing azirines **8** were obtained in excellent to quantitative yields. To the best of our knowledge, this is the first example of the preparation of 2,2,2-trifluoroethyl azirines.

**Scheme 5 Transformations of alkenyl azide product 3 into $CF_3$-containing azirines 8**[a, b]




[a]Reaction condition: **3** (0.2 mmol) in toluene at 110 °C for 6 h - 12 h. [b]Isolated yield. [c]**3** (0.5 mmol).

In summary, we have developed a transition-metal-free and mild procedure for the regioselective azidation of trifluoromethyl alkenyl triflates with $TMSN_3$ under base conditions. From the same starting materials, trifluoromethyl alkenyl triflates and $TMSN_3$, the divergent products, allyl azides and alkenyl azides, were obtained in good to excellent yields with the control of organic amines. This protocol tolerated a wide range of functional groups and avoided the use of expensive and relatively unstable trifluoromethylating reagent. A useful transformation for amines, triazoles, and *2H*-azirines also indicated the synthetic potential of this protocol.

## EXPERIMENTAL SECTION

**General information.** Unless otherwise noted, all reactions were performed under Ar atmosphere in oven-dried glassware with magnetic stirring. All solvents were treated by molecular sieves. Reagents were obtained commercially and used without further purification. Column chromatography was performed on silica gel (200−300 mesh) using petroleum ether/ethyl acetate as an eluent. NMR spectra were recorded in $CDCl_3$ at 400 MHz ($^1H$), 100 MHz or 126 MHz ($^{13}C$), and 377 MHz or 470 MHz ($^{19}F$) on a spectrometer. Chemical shift ($\delta$) were reported in parts per million (ppm) relative to the residual solvent signal. HRMS (EI, ESI and APCI) spectra were measured with quadrupole and TOF mass spectrometers. NaH (60% in mineral oil) was washed with dry *n*-hexane to remove mineral oil prior to use.

### Typical experimental procedure for 1[9d,9f]

The synthesis of **1** was described in Scheme 1. To a suspension of NaH (240 mg, 10.0 mmol, powder) in MTBE (5 mL) was added ethyl trifluoroacetate (1.2 mL, 10.0 mmol) at room temperature under Ar atmosphere. After 1 min of stirring, a solution of ketone (5.0 mmol) in MTBE (5 mL) was added, and the mixture was refluxed for 6 h -12 h. After reaction completed (monitored by TLC and GC analyses), the reaction solution was cooled to 0 ºC. $Tf_2O$ (2.82 g, 10 mmol) was added dropwise to the reaction mixture. After reaction completed (monitored by TLC and GC analyses), the reaction was quenched with ice-water. The aqueous layer was separated and extracted with EtOAc. The combined organic extracts were washed with brine, dried over

$MgSO_4$, and solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel (petroleum ether as eluent) to afford the trifluoromethanesulfonate products.

**Characterization data for new compounds (1c, 1g, 1h, 1j, 1k, 1m and 1o).**

**(*Z*)-4-(4-Isopropylphenyl)-1,1,1-trifluorobut-2-en-2-yl trifluoromethanesulfonate (1c).** This compound was prepared from 3-(4-isopropylphenyl)-1-(4-methoxyphenyl)propan-1-one. Colorless oil; yield 92% (1.73 g); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.22 (d, $J$ = 8.1 Hz, 2H), 7.14 (d, $J$ = 8.0 Hz, 2H), 6.50 (t, $J$ = 7.6 Hz, 1H), 3.66 (d, $J$ = 7.5 Hz, 2H), 2.93 - 2.88 (m, 1H), 1.25 (d, $J$ = 6.9 Hz, 6H). $^{13}$C{$^1$H}NMR (100 MHz, $CDCl_3$) $\delta$ 148.2, 133.8 (q, $J$ = 39.4 Hz), 133.0, 130.3 (q, $J$ = 3.1 Hz), 128.5, 127.2, 118.7 (q, $J$ = 278.3 Hz), 118.5 (q, $J$ = 314.6 Hz), 33.8, 31.8, 23.9. $^{19}$F NMR (377 MHz, $CDCl_3$) $\delta$ -70.44 ~ -70.45 (m, 3F), -73.45 ~ -73.48 (m, 3F). HRMS (APCI) *m/z*: calcd for $C_{14}H_{13}F_6O_3S$ $[M-H]^-$ 375.0495, found: 375.0502.

**(*Z*)-4-(4-Bromophenyl)-1,1,1-trifluorobut-2-en-2-yl trifluoromethanesulfonate (1g).** This compound was prepared from 3-(4-bromophenyl)-1-(4-methoxyphenyl)propan-1-one. Colorless oil; yield 52% (1.07 g); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.48 (d, $J$ = 8.3 Hz, 2H), 7.09 (d, $J$ = 8.3 Hz, 2H), 6.46 (t, $J$ = 7.6 Hz, 1H), 3.64 (d, $J$ = 7.6 Hz, 2H). $^{13}$C{$^1$H}NMR (100 MHz, $CDCl_3$) $\delta$ 134.5, 134.3 (q, $J$ = 39.3 Hz), 132.2, 130.2, 129.2 (q, $J$ = 3.2 Hz), 121.5, 118.6 (q, $J$ = 288.6 Hz), 118.3 (q, $J$ = 304.5 Hz), 31.5. $^{19}$F NMR (377 MHz, $CDCl_3$) $\delta$ -70.44 ~ -70.45 (m, 3F), -73.22 ~ -70.23 (m, 3F). HRMS (APCI) *m/z*: calcd for $C_{11}H_6BrF_6O_3S$

[M-H]$^-$ 410.9131, found: 410.9125.

**(*Z*)-4-(4-Ethoxycarbonylphenyl)-1,1,1-trifluorobut-2-en-2-yl trifluoromethanesulfonate (1h).** This compound was prepared from ethyl 4-(4,4-dimethyl-3-oxopentyl)benzoate. Pale solid; mp 38.8 - 39.0 ºC; yield 78% (1.58 g); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.03 (d, $J$ = 8.4 Hz, 2H), 7.28 (d, $J$ = 8.4 Hz, 2H), 6.49 (t, $J$ = 7.5 Hz, 1H), 4.38 (q, $J$ = 7.1 Hz, 2H), 3.74 (dd, $J$ = 7.5, 1.6 Hz, 2H), 1.40 (t, $J$ = 7.1 Hz, 3H). $^{13}$C{$^1$H}NMR (100 MHz, $CDCl_3$) $\delta$ 166.1, 140.5, 134.5 (q, $J$ = 39.4 Hz), 130.3, 129.8, 129.0 (q, $J$ = 3.3 Hz), 128.5, 118.6 (q, $J$ = 288.9 Hz), 118.3 (q, $J$ = 304.3 Hz), 61.1, 32.0, 14.3. $^{19}$F NMR (377 MHz, $CDCl_3$) $\delta$ -70.43 ~ -70.45 (m, 3F), -73.21 ~ -73.25 (m, 3F). HRMS (APCI) *m/z*: calcd for $C_{14}H_{11}F_6O_5S$ [M-H]$^-$ 405.0237, found: 405.0243.

**(*Z*)-4-[(1,1'-Biphenyl)-4-yl]-1,1,1-trifluorobut-2-en-2-yl trifluoromethanesulfonate (1j).** This compound was prepared from 3-[(1,1'-biphenyl)-4-yl]-1-(4-methoxyphenyl)propan-1-one. White solid; mp 77.9 - 78.1 ºC; yield 49% (1.00 g); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.60 - 7.59 (m, 4H), 7.46 (t, $J$ = 7.6 Hz, 2H), 7.37 (t, $J$ = 7.7 Hz, 1H), 7.29 (d, $J$ = 8.1 Hz, 2H), 6.55 (t, $J$ = 7.4 Hz, 1H), 3.74 (d, $J$ = 7.4, 1.2 Hz, 2H). $^{13}$C{$^1$H}NMR (100 MHz, $CDCl_3$) $\delta$ 140.55, 140.52, 134.6, 134.1 (q, $J$ = 39.3 Hz), 129.9 (q, $J$ = 3.1 Hz), 129.0, 128.9, 127.8, 127.5, 127.1, 118.7 (q, $J$ = 281.4Hz), 118.5 (q, $J$ = 311.5 Hz), 31.8. $^{19}$F NMR (377 MHz, $CDCl_3$) $\delta$ -70.31 ~ -70.33 (m, 3F), -73.17 ~ -73.22 (m, 3F). HRMS (APCI) *m/z*: calcd for $C_{17}H_{11}F_6O_3S$ [M-H]$^-$ 409.0339, found: 409.0345.

**(*Z*)-4-(3-Trifluoromethylphenyl)-1,1,1-trifluorobut-2-en-2-yl**

**trifluoromethanesulfonate (1k).** This compound was prepared from 1-(4-methoxyphenyl)-3-(4-trifluoromethylphenyl)propan-1-one. Colorless oil; yield 91% (1.83 g); $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.58 (d, $J$ = 7.7 Hz, 1H), 7.51 - 7.48 (m, 2H), 7.44 (d, $J$ = 7.7 Hz, 1H), 6.51 (t, $J$ = 7.6 Hz, 1H), 3.78 (d, $J$ = 7.6 Hz, 2H). $^{13}$C{$^{1}$H}NMR (100 MHz, $CDCl_3$) $\delta$ 136.6, 134.6 (q, $J$ = 39.4 Hz), 131.9 (q, $J$ = 0.9 Hz), 131.5 (q, $J$ = 32.4 Hz), 129.6, 128.8 (q, $J$ = 3.2 Hz), 125.2 (q, $J$ = 3.8 Hz), 124.3 (q, $J$ = 3.8 Hz), 121.2 (q, $J$ = 268.0 Hz), 118.6 (q, $J$ = 291.9 Hz), 118.4 (q, $J$ = 300.9 Hz), 31.8. $^{19}$F NMR (377 MHz, $CDCl_3$) $\delta$ -63.61 (s, 3F), -70.83 ~ -70.84 (m, 3F), -73.62 ~ -73.64 (m, 3F). HRMS (APCI) *m/z*: calcd for $C_{12}H_6F_9O_3S$ $[M-H]^-$ 400.9899, found: 400.9907.

**(*Z*)-4-(3-Chloro-2-fluorophenyl)-1,1,1-trifluorobut-2-en-2-yl trifluoromethanesulfonate (1m).** This compound was prepared from 3-(3-chloro-2-fluorophenyl)-1-(4-methoxyphenyl)propan-1-one. Colorless oil; yield 86% (1.66 g); $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.38 - 7.34 (m, 1H), 7.14 - 7.06 (m, 2H), 6.48 (t, $J$ = 7.6 Hz, 1H), 3.73 (d, $J$ = 7.6 Hz, 2H). $^{13}$C{$^{1}$H}NMR (100 MHz, $CDCl_3$) $\delta$ 156.4 (d, $J$ = 248.7 Hz), 134.7 (q, $J$ = 39.5 Hz), 130.2, 128.8 (q, $J$ = 3.4 Hz), 127.8, 125.0 (d, $J$ = 4.8 Hz), 124.3 (d, $J$ = 15.7 Hz), 121.6 (d, $J$ = 17.7 Hz), 118.6 (q, $J$ = 293.3 Hz), 118.3 (q, $J$ = 299.7 Hz), 26.0 (d, $J$ = 3.0 Hz). $^{19}$F NMR (377 MHz, $CDCl_3$) $\delta$ -70.64 ~ -70.65 (m, 3F), -73.36 ~ -73.40 (m, 3F), -119.85 ~ -119.88 (m, 1F). HRMS (APCI) *m/z*: calcd for $C_{11}H_5ClF_7O_3S$ $[M-H]^-$ 384.9542, found: 384.9549.

**(*Z*)-4-(2-Chloro-4-fluorophenyl)-1,1,1-trifluorobut-2-en-2-yl trifluoromethanesulfonate (1o).** This compound was prepared from

3-(2-chloro-4-fluorophenyl)-1-(4-methoxyphenyl)propan-1-one. Colorless oil; yield 82%(1.59 g); $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.28 - 7.22 (m, 2H), 7.06 - 7.02 (m, 1H), 6.35 (t, $J$ = 7.2 Hz, 1H), 3.85 (d, $J$ = 7.2 Hz, 2H). $^{13}$C{$^{1}$H}NMR (100 MHz, $CDCl_3$) $\delta$ 161.3 (d, $J$ = 249.6 Hz), 135.3 (d, $J$ = 5.1 Hz), 134.5 (q, $J$ = 39.4 Hz), 129.6 (d, $J$ = 9.6 Hz), 127.2 (q, $J$ = 3.0 Hz), 125.6 (d, $J$ = 3.4 Hz), 121.9 (d, $J$ = 18.2 Hz), 118.6 (q, $J$ = 291.1 Hz), 118.4 (q, $J$ = 302.0 Hz), 114.4 (d, $J$ = 22.5 Hz), 23.4 (d, $J$ = 3.8 Hz). $^{19}$F NMR (470 MHz, $CDCl_3$) $\delta$ -69.93 (q, $J$ = 4.4 Hz, 3F), -72.71 (q, $J$ = 4.4 Hz, 3F); -112.55 (br, F). HRMS (EI) *m/z*: calcd for $C_{11}H_6ClF_7O_3S$ [$M^{+\cdot}$] 385.9614, found: 385.9620.

**Typical experimental procedure for 2**

Under Ar atmosphere, a solution of **1** (0.2 mmol), $TMSN_3$ (0.4 mmol), $Et_3N$ (15 mol%) and $KHCO_3$ (0.24 mmol) in dry DME (2 mL) was stirred at 65 ºC for 12 h. After the reaction was complete (monitored by TLC and GC analyses), the reaction was quenched with water. The aqueous layer was separated and extracted with EtOAc. The combined organic extracts were washed with brine, dried over $MgSO_4$, and solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel to afford the goal products.

**(*E*)-3-Azido-1-phenyl-4,4,4-trifluorobut-1-ene (2a).** Colorless oil; yield 90% (102 mg); $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.49 - 7.47 (m, 2H), 7.44 - 7.38 (m, 3H), 6.90 (d, $J$ = 15.8 Hz, 1H), 6.18 (dd, $J$ = 15.8, 8.0 Hz, 1H), 4.52 - 4.45 (m, 1H). $^{13}$C{$^{1}$H}NMR (100 MHz, $CDCl_3$) $\delta$ 139.2, 134.8, 129.3, 128.9, 127.1, 123.8 (q, $J$ = 281.2 Hz), 116.4, 63.9 (q, $J$ = 31.5 Hz). $^{19}$F NMR (377 MHz, $CDCl_3$) $\delta$-75.35 (d, $J$ = 6.7 Hz). HRMS

(ESI) *m/z*: calcd for $C_{20}H_{17}F_6N_6$ $[2M+H]^+$ 455.1419, found: 455.1421.

**(*E*)-3-Azido-1-(4-methylphenyl)-4,4,4-trifluorobut-1-ene (2b).** Colorless oil; yield 69% (42 mg); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.39 (d, $J$ = 7.9 Hz, 2H), 7.23 (d, $J$ = 7.9 Hz, 2H), 6.87 (d, $J$ = 15.8 Hz, 1H), 6.17 - 6.11 (m, 1H), 4.50 - 4.43 (m, 1H), 2.42 (s, 3H). $^{13}$C{$^1$H}NMR (100 MHz, $CDCl_3$) $\delta$ 139.4, 139.2, 132.0, 129.5, 127.0, 123.7 (q, $J$ = 281.2 Hz), 115.3, 64.0 (q, $J$ = 31.5 Hz), 21.3. $^{19}$F NMR (377 MHz, $CDCl_3$) $\delta$ -75.22 (d, $J$ = 6.6 Hz). HRMS (ESI) *m/z*: calcd for $C_{22}H_{21}F_6N_6$ $[2M+H]^+$ 483.1732, found: 483.1745.

**(*E*)-3-Azido-1-(4-isopropylphenyl)-4,4,4-trifluorobut-1-ene (2c).** Colorless oil; yield 77% (52 mg); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.42 (d, $J$ = 8.1 Hz, 2H), 7.28 (d, $J$ = 8.1 Hz, 2H), 6.89 (d, $J$ = 15.8 Hz, 1H), 6.14 (dd, $J$ = 15.8, 8.1 Hz, 1H), 4.51 - 4.44 (m, 1H), 3.01 - 2.91 (m, 1H), 1.30 (d, $J$ = 6.9 Hz, 6H). $^{13}$C{$^1$H}NMR (100 MHz, $CDCl_3$) $\delta$ 150.4, 139.2, 132.4, 127.1, 127.0, 123.7 (q, $J$ = 281.1 Hz), 115.4 (q, $J$ = 1.7 Hz), 64.0 (q, $J$ = 31.6 Hz), 34.0, 23.9. $^{19}$F NMR (377 MHz, $CDCl_3$) $\delta$ -75.41 (d, $J$ = 6.7 Hz). HRMS (ESI) *m/z*: calcd for $C_{26}H_{29}F_6N_6$ $[2M+H]^+$ 539.2358, found: 539.2358.

**(*E*)-3-Azido-1-(4-methoxyphenyl)-4,4,4-trifluorobut-1-ene (2d).** Colorless oil; yield 82% (53 mg); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.41 (d, $J$ = 8.6 Hz, 2H), 6.93 (d, $J$ = 8.6 Hz, 2H), 6.83 (d, $J$ = 15.8 Hz, 1H), 6.02 (dd, $J$ = 15.8, 8.2 Hz, 1H), 4.49 - 4.41 (m, 1H), 3.85 (s, 3H). $^{13}$C{$^1$H}NMR (100 MHz, $CDCl_3$) $\delta$ 160.5, 138.8, 128.5, 127.4, 123.7 (q, $J$ = 281.1 Hz), 114.2, 113.9 (q, $J$ = 1.6 Hz), 64.1 (q, $J$ = 31.5 Hz), 55.3. $^{19}$F NMR (377 MHz, $CDCl_3$) $\delta$ -75.45 (d, $J$ = 6.6 Hz). HRMS (ESI) *m/z*: calcd for

$C_{22}H_{21}F_6N_6O_2$ $[2M+H]^+$ 515.1630, found: 515.1636.

**(*E*)-3-Azido-1-(4-fluorophenyl)-4,4,4-trifluorobut-1-ene (2e).** Colorless oil; yield 81% (99 mg); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.46 - 7.41 (m, 2H), 7.08 (t, $J$ = 8.6 Hz, 2H), 6.85 (d, $J$ = 15.8 Hz, 1H), 6.07 (dd, $J$ = 15.8, 8.0 Hz, 1H), 4.50 - 4.44 (m, 1H). $^{13}$C{$^1$H}NMR (100 MHz, $CDCl_3$) $\delta$ 163.3 (d, $J$ = 249.4 Hz), 137.9, 131.0 (d, $J$ = 3.4 Hz), 128.8 (d, $J$ = 8.3 Hz), 123.7 (q, $J$ = 281.3 Hz), 116.2, 115.9 (d, $J$ = 21.9 Hz), 63.8 (q, $J$ = 31.6 Hz). $^{19}$F NMR (377 MHz, $CDCl_3$) $\delta$ -75.42 (d, $J$ = 6.6 Hz, 3F), -112.09 ~ -112.16 (m, F). HRMS (ESI) *m/z*: calcd for $C_{20}H_{15}F_8N_6$ $[2M+H]^+$ 491.1230, found: 491.1237.

**(*E*)-3-Azido-1-(4-chlorophenyl)-4,4,4-trifluorobut-1-ene (2f).** Colorless oil; yield 87% (57 mg); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.37 (d, $J$ = 8.7 Hz, 2H), 7.34 (d, $J$ = 8.7 Hz, 2H), 6.83 (d, $J$ = 15.8 Hz, 1H), 6.11 (dd, $J$ = 15.8, 7.8 Hz, 1H), 4.49 - 4.43 (m, 1H). $^{13}$C{$^1$H}NMR (100 MHz, $CDCl_3$) $\delta$ 137.7, 135.1, 133.2, 129.1, 128.3, 123.6 (q, $J$ = 281.4 Hz), 117.2 (q, $J$ = 1.5 Hz), 63.7 (q, $J$ = 31.5 Hz). $^{19}$F NMR (377 MHz, $CDCl_3$) $\delta$ -75.30 (d, $J$ = 4.6 Hz). HRMS (ESI) *m/z*: calcd for $C_{20}H_{15}Cl_2F_6N_6$ $[2M+H]^+$523.0639, found: 523.0641.

**(*E*)-3-Azido-1-(4-bromophenyl)-4,4,4-trifluorobut-1-ene (2g).** Colorless oil; yield 85% (65 mg); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.51 (d, $J$ = 8.4 Hz, 2H), 7.31 (d, $J$ = 8.4 Hz, 2H), 6.82 (d, $J$ = 15.8 Hz, 1H), 6.13 (dd, $J$ = 15.8, 7.8 Hz, 1H), 4.50 - 4.43 (m, 1H). $^{13}$C{$^1$H}NMR (100 MHz, $CDCl_3$) $\delta$ 137.8, 133.7, 132.0, 128.5, 123.6 (q, $J$ = 281.4 Hz), 123.3, 117.3 (q, $J$ = 1.5 Hz), 63.7 (q, $J$ = 31.5 Hz). $^{19}$F NMR (377 MHz, $CDCl_3$) $\delta$ -75.27 (d, $J$ = 6.6 Hz). HRMS (ESI) *m/z*: calcd for $C_{20}H_{15}Br_2F_6N_6$ $[2M+H]^+$

612.9609, found: 612.9620.

**(*E*)-Ethyl 4-(3-azido-4,4,4-trifluorobut-1-enyl)benzoate (2h).** Colorless oil; yield 48% (36 mg); $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.99 (d, $J$ = 8.3 Hz, 2H), 7.44 (d, $J$ = 8.3 Hz, 2H), 6.85 (d, $J$ = 15.8 Hz, 1H), 6.17 (dd, $J$ = 15.8, 7.7 Hz, 1H), 4.48 - 4.41 (m, 1H), 4.33 (q, $J$ = 7.1 Hz, 2H), 1.35 (t, $J$ = 7.1 Hz, 3H). $^{13}$C{$^{1}$H}NMR (100 MHz, $CDCl_3$) $\delta$ 166.1, 138.9, 137.8, 130.9, 130.1, 126.9, 123.6 (q, $J$ = 281.4 Hz), 119.0 (q, $J$ = 1.6 Hz), 63.6 (q, $J$ = 31.6 Hz), 61.2, 14.3. $^{19}$F NMR (377 MHz, $CDCl_3$) $\delta$ -75.19 (d, $J$ = 6.5 Hz). HRMS (EI) *m/z*: calcd for $C_{13}H_{12}N_3O_2F_3$ [$M^{+\cdot}$] 299.0882, found: 299.0872.

**(*E*)-3-Azido-1-(4-cyanophenyl)-4,4,4-trifluorobut-1-ene (2i).** Colorless oil; yield 23% (12 mg); $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.69 (d, $J$ = 8.2 Hz, 2H), 7.56 (d, $J$ = 8.2 Hz, 2H), 6.92 (d, $J$ = 15.9 Hz, 1H), 6.26 (dd, $J$ = 15.9, 7.4 Hz, 1H), 4.58 - 4.51 (m, 1H). $^{13}$C{$^{1}$H}NMR (100 MHz, $CDCl_3$) $\delta$ 139.1, 136.8, 132.6, 127.6, 123.5 (q, $J$ = 281.7 Hz), 120.5 (q, $J$ = 1.3 Hz), 118.4, 112.6, 63.4 (q, $J$ = 31.6 Hz). $^{19}$F NMR (377 MHz, $CDCl_3$) $\delta$ -75.09 (d, $J$ = 6.6 Hz). HRMS (EI) *m/z*: calcd for $C_{11}H_7N_4F_3$ [$M^{+\cdot}$] 252.0623, found: 252.0616.

**(*E*)-3-Azido-1-[(1,1'-biphenyl)-4-yl]-4,4,4-trifluorobut-1-ene (2j).** White solid; mp 91.9 – 92.1 ºC; yield 87% (66 mg); $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.67 (d, $J$ = 8.0 Hz, 4H), 7.56 (d, $J$ = 8.2 Hz, 2H), 7.53 - 7.50 (m, 2H), 7.45 - 7.41 (m, 1H), 6.95 (d, $J$ = 15.8 Hz, 1H), 6.23 (dd, $J$ = 15.8, 8.0 Hz, 1H), 4.56 - 4.49 (m, 1H). $^{13}$C{$^{1}$H}NMR (100 MHz, $CDCl_3$) $\delta$ 142.1, 140.3, 138.7, 133.7, 128.9, 127.8, 127.6, 127.5, 127.1, 123.8 (q, $J$ = 281.1 Hz), 116.4 (q, $J$ = 1.5 Hz), 63.9 (q, $J$ = 31.6 Hz). $^{19}$F NMR (377 MHz,

$CDCl_3$) $\delta$ -75.26 (d, $J$ = 6.2 Hz). HRMS (EI) *m/z*: calcd for $C_{16}H_{12}N_3F_3$ [$M^{+\cdot}$] 303.0983, found: 303.0994.

**(*E*)-3-Azido-1-(3-trifluoromethylphenyl)-4,4,4-trifluorobut-1-ene (2k).** Colorless oil; yield 78% (57 mg); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.68 (s, 1H), 7.63 - 7.59 (m, 2H), 7.52 - 7.48 (m, 1H), 6.92 (d, $J$ = 15.9 Hz, 1H), 6.20 (dd, $J$ = 15.9, 7.6 Hz, 1H), 4.54 - 4.47 (m, 1H). $^{13}$C{$^1$H}NMR (100 MHz, $CDCl_3$) $\delta$ 137.3, 135.5, 131.4 (q, $J$ = 32.6 Hz), 130.1 (q, $J$ = 0.9 Hz), 129.4, 125.7 (q, $J$ = 3.7 Hz), 123.9 (q, $J$ = 272.4 Hz), 123.8 (q, $J$ = 3.8 Hz), 123.6 (q, $J$ = 281.5 Hz), 118.6 (q, $J$ = 1.5 Hz), 63.6 (q, $J$ = 31.7 Hz). $^{19}$F NMR (377 MHz, $CDCl_3$) $\delta$ -63.33 (s, 3F); -75.26 (d, $J$ = 6.4 Hz, 3F). HRMS (ESI) *m/z*: calcd for $C_{22}H_{15}F_{12}N_6$ $[2M+H]^+$ 591.1167, found: 591.1171.

**(*E*)-3-Azido-1-(3-chlorophenyl)-4,4,4-trifluorobut-1-ene (2l).** Colorless oil; yield 75% (98 mg); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.44 (s, 1H), 7.31 - 7.28 (m, 3H), 6.82 (d, $J$ = 15.8 Hz, 1H), 6.15 (d, $J$ = 15.8, 7.8 Hz, 1H), 4.51 - 4.44 (m, 1H). $^{13}$C{$^1$H}NMR (100 MHz, $CDCl_3$) $\delta$ 137.5, 136.6, 134.9, 130.1, 129.2, 126.9, 125.3, 123.6 (q, $J$ = 281.4 Hz), 118.1 (q, $J$ = 1.6 Hz), 63.6 (q, $J$ = 31.6 Hz). $^{19}$F NMR (377 MHz, $CDCl_3$) $\delta$ -75.09 (d, $J$ = 6.5 Hz). HRMS (ESI) *m/z*: calcd for $C_{20}H_{15}Cl_2F_6N_6$ $[2M+H]^+$ 523.0639, found: 523.0658.

**(*E*)-3-Azido-1-(3-chloro-2-fluorophenyl)-4,4,4-trifluorobut-1-ene (2m).** Colorless oil; yield 80% (56 mg); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.41 - 7.38 (m, 2H), 7.13 - 7.09 (m, 1H), 7.02 (d, $J$ = 16.0 Hz, 1H), 6.27 (dd, $J$ = 16.0, 7.7 Hz, 1H), 4.56 - 4.49 (m, 1H). $^{13}$C{$^1$H}NMR (100 MHz, $CDCl_3$) $\delta$ 155.9 (d, $J$ = 253.4 Hz), 131.0, 130.8 (d, $J$ = 3.2 Hz), 126.2 (d, $J$ = 2.6 Hz), 124.7 (d, $J$ = 4.8 Hz), 124.3 (d, $J$ = 12.0 Hz), 123.6

(q, $J$ = 281.5 Hz), 122.0 (d, $J$ = 18.0 Hz), 120.6 (dd, $J$ = 5.7, 1.6 Hz), 63.8 (q, $J$ = 31.6 Hz). $^{19}$F NMR (377 MHz, $CDCl_3$) $\delta$ -75.25 (d, $J$ = 6.5 Hz, 3F), -119.07 ~ -119.11 (m, F). HRMS (ESI) *m/z*: calcd for $C_{20}H_{13}Cl_2F_8N_6$ $[2M+H]^+$ 559.0451, found: 559.0454.

**(*E*)-3-Azido-1-(2-chlorophenyl)-4,4,4-trifluorobut-1-ene (2n).** Colorless oil; yield 91% (60 mg); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.59 - 7.56 (m, 1H), 7.43 - 7.40 (m, 1H), 7.32 - 7.27 (m, 3H), 6.14 (dd, $J$ = 15.8, 7.9 Hz, 1H), 4.57 - 4.50 (m, 1H). $^{13}$C{$^1$H}NMR (100 MHz, $CDCl_3$) $\delta$ 135.3, 133.7, 133.1, 130.2, 130.0, 127.3, 127.1, 123.6 (q, $J$ = 281.4 Hz), 119.3 (q, $J$ = 1.5 Hz), 63.7 (q, $J$ = 31.5 Hz). $^{19}$F NMR (377 MHz, $CDCl_3$) $\delta$ -75.26 (d, $J$ = 6.7 Hz). HRMS (ESI) m/z: calcd for $C_{20}H_{15}Cl_2F_6N_6$ $[2M+H]^+$ 523.0639, found: 523.0642.

**(*E*)-3-Azido-1-(2-chloro-4-fluorophenyl)-4,4,4-trifluorobut-1-ene (2o).** Colorless oil; yield 90% (63 mg); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.28 - 7.21 (m, 2H), 7.09 - 7.02 (m, 2H), 6.44 (dd, $J$ = 16.2, 7.7 Hz, 1H), 4.56 - 4.49 (m, 1H). $^{13}$C{$^1$H}NMR (100 MHz, $CDCl_3$) $\delta$ 161.3 (d, $J$ = 254.2 Hz), 134.9 (d, $J$ = 5.2 Hz), 129.9 (d, $J$ = 10.3 Hz), 129.2, 125.8 (d, $J$ = 3.5 Hz), 124.3 (m), 123.6 (q, $J$ = 281.5 Hz), 121.8 (d, $J$ = 14.3 Hz), 114.8 (d, $J$ = 23.3 Hz), 64.3 (q, $J$ = 31.5 Hz). $^{19}$F NMR (377 MHz, $CDCl_3$) $\delta$ -75.23 (d, $J$ = 6.4 Hz, 3F), -110.58 ~ -110.61 (m, F). HRMS (ESI) *m/z*: calcd for $C_{20}H_{13}Cl_2F_8N_6$ $[2M+H]^+$ 559.0451, found: 559.0456.

**(*E*)-3-Azido-1-(1-naphthaleneyl)-4,4,4-trifluorobut-1-ene (2p).** Colorless oil; yield 90% (63 mg); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.11 (d, $J$ = 8.2 Hz, 1H), 7.95 - 7.90 (m, 2H), 7.69 - 7.57 (m, 4H), 7.54 - 7.50 (m, 1H), 6.24 (dd, $J$ = 15.5, 7.8 Hz, 1H), 4.63 - 4.56 (m, 1H). $^{13}$C{$^1$H}NMR (100 MHz, $CDCl_3$) $\delta$ 136.7, 133.6, 132.6, 131.0, 129.5,

128.8, 126.7, 126.2, 125.6, 124.7, 123.8 (q, $J$ = 281.4 Hz), 123.4, 119.7 (q, $J$ = 1.6 Hz), 63.8 (q, $J$ = 31.5 Hz). $^{19}$F NMR (377 MHz, $CDCl_3$) $\delta$ -75.12 (d, $J$ = 6.6 Hz). HRMS (ESI) *m/z*: calcd for $C_{28}H_{21}F_6N_6$ $[2M+H]^+$ 555.1732, found: 555.1734.

**(*E*)-3-Azido-1-(3,4,5-trimethoxyphenyl)-4,4,4-trifluorobut-1-ene (2q).** Pale yellow solid; mp 59.0 - 59.2 ºC; yield 95% (76 mg); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 6.77 (d, $J$ = 15.7 Hz, 1H), 6.64 (s, 2H), 6.01 (dd, $J$ = 15.7, 8.0 Hz, 1H), 4.48 - 4.41 (m, 1H), 3.87 (s, 6H), 3.84 (s, 3H). $^{13}$C{$^1$H}NMR (100 MHz, $CDCl_3$) $\delta$ 153.5, 139.1, 130.3, 123.7 (q, $J$ = 281.5 Hz), 115.7 (q, $J$ = 1.5 Hz), 104.2, 63.8 (q, $J$ = 31.6 Hz), 60.9, 56.1. $^{19}$F NMR (377 MHz, $CDCl_3$) $\delta$ -75.42 (d, $J$ = 6.6 Hz). HRMS (ESI) *m/z*: calcd for $C_{13}H_{15}F_3N_3O_3$ $[M+H]^+$ 318.1066, found: 318.1069.

**(*E*)-3-Azido-1-(2-furanyl)-4,4,4-trifluorobut-1-ene (2r).** Colorless oil; yield 48% (52 mg); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.45 (s, 1H), 6.69 (d, $J$ = 15.7 Hz, 1H), 6.45 (s, 2H), 6.10 (dd, $J$ = 15.7, 7.9 Hz, 1H), 4.47 - 4.40 (m, 1H). $^{13}$C{$^1$H}NMR (100 MHz, $CDCl_3$) $\delta$ 150.5, 143.4, 126.3, 123.6 (q, $J$ = 281.4 Hz), 114.5 (q, $J$ = 1.7 Hz), 111.7, 111.3, 63.5 (q, $J$ = 31.7 Hz). $^{19}$F NMR (377 MHz, $CDCl_3$) $\delta$ -75.40 (d, $J$ = 6.5 Hz). HRMS (EI) *m/z*: calcd for $C_8H_6N_3OF_3$ $[M^{+\cdot}]$ 217.0463, found: 217.0456.

**Typical experimental procedure for the compound 3**

Under Ar atmosphere, to a solution of **1** (0.5 mmol), $TMSN_3$ (2.5 mmol) and KF (0.6 mmol) in dry $CH_2Cl_2$ (2.5 mL) was added DBU (1.0 mmol, diluted with 2.5 mL $CH_2Cl_2$) slowly. The resulting mixture was stirred for 1-2 h at room temperature. After the reaction was complete (monitored by TLC and GC analysis), the reaction was quenched with water. The aqueous layer was separated and extracted with EtOAc.

The combined organic extracts were washed with brine, dried over $MgSO_4$, and solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel to afford the goal products.

**(*Z*)-1-Azido-1-phenyl-4,4,4-trifluorobut-1-ene (3a).** Colorless oil; yield 63% (71 mg); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.50 - 7.43 (m, 5H), 5.14 (t, $J$ = 7.2 Hz, 1H), 3.15 (qd, $J$ = 10.8, 7.2 Hz, 2H). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) $\delta$ 142.4, 134.1, 129.5, 128.9, 127.2, 126.0 (q, $J$ = 276.6 Hz), 106.6 (q, $J$ = 3.6 Hz), 32.2 (q, $J$ = 30.5 Hz). $^{19}$F NMR (377 MHz, $CDCl_3$) $\delta$ -66.47 (t, $J$ = 10.8 Hz). HRMS (EI) *m/z*: calcd for $C_{10}H_8NF_3$ $[M\text{-}N_2]^+$ 199.0609, found: 199.0615.

**(*Z*)-1-Azido-1-(4-methylphenyl)-4,4,4-trifluorobut-1-ene (3b).** Colorless oil; yield 68% (81 mg); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.27 (d, $J$ = 8.2 Hz, 2H), 7.23 (d, $J$ = 8.2 Hz, 2H), 5.02 (t, $J$ = 7.2 Hz, 1H), 3.06 (qd, $J$ = 10.8, 7.2 Hz, 2H), 2.39 (s, 3H). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) $\delta$ 142.3, 139.6, 131.3, 129.5, 127.1, 126.0 (q, $J$ = 276.6 Hz), 106.0 (q, $J$ = 3.6 Hz), 32.2 (q, $J$ = 30.5 Hz), 21.2. $^{19}$F NMR (377 MHz, $CDCl_3$) $\delta$ -66.53 (t, $J$ = 10.8 Hz). HRMS (EI) *m/z*: calcd for $C_{11}H_{10}N_3F_3$ $[M^{+\cdot}]$ 241.0827, found: 241.0835.

**(*Z*)-1-Azido-1-(4-isopropylphenyl)-4,4,4-trifluorobut-1-ene (3c).** Colorless oil; yield 67% (89 mg); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.31 (d, $J$ = 8.5 Hz, 2H), 7.28 (d, $J$ = 8.5 Hz, 2H), 5.03 (t, $J$ = 7.2 Hz, 1H), 3.07 (qd, $J$ = 10.8, 7.2 Hz, 2H), 2.97 - 2.91 (m, 1H), 1.27 (d, $J$ = 6.9 Hz, 6H). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) $\delta$ 150.5, 142.3, 131.6, 127.2, 126.9, 126.0 (q, $J$ = 276.6 Hz), 106.1 (t, $J$ = 3.7 Hz), 34.0, 32.2 (q, $J$ = 30.5 Hz), 23.8. $^{19}$F NMR (377 MHz, $CDCl_3$) $\delta$ -66.54 (t, $J$ = 10.8 Hz). HRMS (EI) *m/z*: calcd

for $C_{13}H_{14}N_3F_3$ [$M^{+\cdot}$] 269.1140, found: 269.1148.

**(*Z*)-1-Azido-1-(4-methoxyphenyl)-4,4,4-trifluorobut-1-ene (3d).** Colorless oil; yield 79% (101 mg); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.32 (d, $J$ = 8.8 Hz, 2H), 6.94 (d, $J$ = 8.8 Hz, 2H), 4.99 (t, $J$ = 7.2 Hz, 1H), 3.84 (s, 3H), 3.06 (qd, $J$ = 10.8, 7.2 Hz, 2H). $^{13}$C{$^1$H}NMR (100 MHz, $CDCl_3$) $\delta$ 160.5, 142.0, 128.6, 126.6, 126.0 (q, $J$ = 276.6 Hz), 114.2, 105.5 (q, $J$ = 3.6 Hz), 55.3, 32.1 (q, $J$ = 30.5 Hz). $^{19}$F NMR (377 MHz, $CDCl_3$) $\delta$ -66.56 (t, $J$ = 10.8 Hz). HRMS (EI) *m/z*: calcd for $C_{11}H_{10}N_3OF_3$ [$M^{+\cdot}$] 257.0776, found: 257.0786.

**(*Z*)-1-Azido-1-(4-fluorophenyl)-4,4,4-trifluorobut-1-ene (3e).** Colorless oil; yield 58% (71 mg); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.39 - 7.36 (m, 2H), 7.15 - 7.11 (m, 2H), 5.03 (t, $J$ = 7.2 Hz, 1H), 3.07 (qd, $J$ = 10.8, 7.2 Hz, 2H).$^{13}$C{$^1$H}NMR (100 MHz, $CDCl_3$) $\delta$ 163.3 (d, $J$ = 249.8 Hz), 141.4, 130.2 (d, $J$ = 3.4 Hz), 129.2 (d, $J$ = 8.4 Hz), 125.9 (q, $J$ = 276.6 Hz), 116.0 (d, $J$ = 21.9 Hz), 106.8 (q, $J$ = 3.7 Hz), 32.1 (q, $J$ = 30.6 Hz). $^{19}$F NMR (377 MHz, $CDCl_3$) $\delta$ -66.53 (t, $J$ = 10.8 Hz, 3F), -111.50 ~ -111.57 (m, F). HRMS (EI) *m/z*: calcd for $C_{10}H_7N_3F_4$ [$M^{+\cdot}$] 245.0576, found: 245.0584.

**(*Z*)-1-Azido-1-(4-chlorophenyl)-4,4,4-trifluorobut-1-ene (3f).** Colorless oil; yield 77% (100 mg); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.42 (d, $J$ = 8.6 Hz, 2H), 7.33 (d, $J$ = 8.6 Hz, 2H), 5.07 (t, $J$ = 7.2 Hz, 1H), 3.07 (qd, $J$ = 10.8, 7.2 Hz, 2H). $^{13}$C{$^1$H}NMR (100 MHz, $CDCl_3$) $\delta$ 141.3, 135.6, 132.5, 129.2, 128.5, 125.8 (q, $J$ = 276.7 Hz), 107.2 (q, $J$ = 3.7 Hz), 32.1 (q, $J$ = 30.7 Hz). $^{19}$F NMR (377 MHz, $CDCl_3$) $\delta$ -66.48 (t, $J$ = 10.8 Hz). HRMS (EI) *m/z*: calcd for $C_{10}H_7NF_3Cl$ [M-$N_2$]$^+$ 233.0219, found: 233.0230.

**(*Z*)-1-Azido-1-(4-bromophenyl)-4,4,4-trifluorobut-1-ene (3g).** Colorless oil; yield 68% (103 mg); $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.60 (d, $J$ = 8.4 Hz, 2H), 7.29 (d, $J$ = 8.4 Hz, 2H), 5.11 (t, $J$ = 7.2 Hz, 1H), 3.10 (qd, $J$ = 10.8, 7.2 Hz, 2H). $^{13}$C{$^{1}$H}NMR (100 MHz, $CDCl_3$) $\delta$ 141.4, 132.9, 132.2, 128.8, 125.8 (q, $J$ = 276.7 Hz), 123.8, 107.3 (q, $J$ = 3.6 Hz), 32.2 (q, $J$ = 30.6 Hz). $^{19}$F NMR (377 MHz, $CDCl_3$) $\delta$ -66.43 (t, $J$ = 10.8 Hz). HRMS (EI) *m/z*: calcd for $C_{10}H_7NBrF_3$ $[M\text{-}N_2]^+$ 276.9714, found: 276.9708.

**(*Z*)-Ethyl 4-(1-azido-4,4,4-trifluorobut-1-enyl)benzoate (3h).** Colorless oil; yield 77% (115 mg). $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.11 (d, $J$ = 8.6 Hz, 2H), 7.46 (d, $J$ = 8.6 Hz, 2H), 5.16 (t, $J$ = 7.2 Hz, 1H), 4.40 (q, $J$ = 7.1 Hz, 2H), 3.10 (qd, $J$ = 10.8, 7.2 Hz, 2H), 1.41 (t, $J$ = 7.1 Hz, 3H). $^{13}$C{$^{1}$H}NMR (100 MHz, $CDCl_3$) $\delta$ 165.8, 141.5, 138.0, 131.5, 130.1, 127.1, 125.8 (q, $J$ = 276.6 Hz), 108.0 (q, $J$ = 3.7 Hz), 61.2, 32.1 (q, $J$ = 30.7 Hz), 14.2. $^{19}$F NMR (377 MHz, $CDCl_3$) $\delta$ -66.39 (t, $J$ = 10.8 Hz). HRMS (EI) *m/z*: calcd for $C_{13}H_{12}N_3O_2F_3$ $[M^{+\cdot}]$ 299.0882, found: 299.0892.

**(*Z*)-1-Azido-1-(4-cyanophenyl)-4,4,4-trifluorobut-1-ene (3i).** Colorless oil; yield 55% (69 mg). $^{1}$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.75 (d, $J$ = 8.5 Hz, 2H), 7.52 (d, $J$ = 8.5 Hz, 2H), 5.20 (t, $J$ = 7.2 Hz, 1H), 3.12 (qd, $J$ = 10.7, 7.2 Hz, 2H). $^{13}$C{$^{1}$H}NMR (100 MHz, $CDCl_3$) $\delta$ 140.8, 138.2, 132.8, 127.8, 125.6 (q, $J$ = 276.8 Hz), 118.0, 113.4, 109.3 (q, $J$ = 3.5 Hz), 32.3 (q, $J$ = 30.9 Hz). $^{19}$F NMR (377 MHz, $CDCl_3$) $\delta$ -66.31 (t, $J$ = 10.7 Hz). HRMS (EI) *m/z*: calcd for $C_{11}H_7N_2F_3$ $[M\text{-}N_2]^+$ 224.0561, found: 224.0571.

**(*Z*)-1-Azido-1-[(1,1'-biphenyl)-4-yl]-4,4,4-trifluorobut-1-ene (3j).** White solid; mp 71.9 – 73.0 ºC; yield 60% (91 mg). $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.72 - 7.65 (m, 4H),

7.53 - 7.41 (m, 5H), 5.18 (t, $J$ = 7.2 Hz, 1H), 3.16 (qd, $J$ = 10.8, 7.2 Hz, 2H). $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) $\delta$ 142.4, 142.1, 140.1, 132.9, 129.0, 127.9, 127.63, 127.58, 127.2, 126.0 (q, $J$ = 276.7 Hz), 106.7 (q, $J$ = 3.6 Hz), 32.3 (q, $J$ = 30.5 Hz). $^{19}F$ NMR (377 MHz, $CDCl_3$) $\delta$ -66.36 (t, $J$ = 10.8 Hz). HRMS (EI) *m/z*: calcd for $C_{16}H_{12}N_3F_3$ $[M^{+\cdot}]$ 303.0983, found: 303.0987.

**(*Z*)-1-Azido-1-(3-trifluoromethylphenyl)-4,4,4-trifluorobut-1-ene (3k).** Colorless oil; yield 64% (94 mg); $^{1}H$ NMR (500 MHz, $CDCl_3$) $\delta$ 7.70 - 7.69 (m, 1H), 7.65 (s, 1H), 7.59 - 7.58 (m, 2H), 5.15 (t, $J$ = 7.2 Hz, 1H), 3.11 (qd, $J$ = 10.7, 7.2 Hz, 2H). $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) $\delta$ 141.1, 134.8, 131.6 (q, $J$ = 32.8 Hz), 130.4, 129.5, 126.3 (q, $J$ = 3.7 Hz), 125.7 (q, $J$ = 276.6 Hz), 124.2 (q, $J$ = 3.8 Hz), 123.7 (q, $J$ = 272.5 Hz), 108.2 (q, $J$ = 3.6 Hz), 32.1 (q, $J$ = 30.8 Hz). $^{19}F$ NMR (377 MHz, $CDCl_3$) $\delta$ -63.42 (s, 3F), -66.51 (t, $J$ = 10.7 Hz, 3F). HRMS (EI) *m/z*: calcd for $C_{11}H_7NF_6$ $[M\text{-}N_2]^+$ 267.0483, found: 267.0472.

**(*Z*)-1-Azido-1-(3-chlorophenyl)-4,4,4-trifluorobut-1-ene (3l).** Colorless oil; yield 69% (90 mg); $^{1}H$ NMR (500 MHz, $CDCl_3$) $\delta$ 7.42 - 7.36 (m, 3H), 7.28 - 7.26 (m, 1H), 5.10 (t, $J$ = 7.2 Hz, 1H), 3.08 (qd, $J$ = 10.7, 7.2 Hz, 2H). $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) $\delta$ 141.1, 135.7, 135.0, 130.2, 129.7, 127.5, 125.8 (q, $J$ = 276.7), 125.3, 107.7 (q, $J$ = 3.6 Hz), 32.1 (q, $J$ = 30.7 Hz). $^{19}F$ NMR (377 MHz, $CDCl_3$) $\delta$ -66.44 (t, $J$ = 10.7 Hz). HRMS (EI) *m/z*: calcd for $C_{10}H_7NF_3Cl$ $[M\text{-}N_2]^+$ 233.0219, found: 233.0214.

**(*Z*)-1-Azido-1-(3-chloro-2-fluorophenyl)-4,4,4-trifluorobut-1-ene (3m).** Colorless oil; yield 67% (93 mg). $^{1}H$ NMR (500 MHz, $CDCl_3$) $\delta$ 7.51 - 7.47 (m, 1H), 7.26 - 7.22 (m, 1H), 7.19 - 7.15 (m, 1H), 5.05 (t, $J$ = 7.2 Hz, 1H), 3.09 (qd, $J$ = 10.7, 7.2 Hz,

2H). $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) $\delta$ 155.10 (d, $J$ = 252.0 Hz), 136.3, 132.2, 128.9 (d, $J$ = 2.2 Hz), 125.7 (q, $J$ = 276.6 Hz), 125.1 (d, $J$ = 4.8 Hz), 123.3 (d, $J$ = 15.3 Hz), 122.1 (d, $J$ = 18.0 Hz), 109.5 (q, $J$ = 3.4 Hz), 32.0 (q, $J$ = 30.8 Hz). $^{19}F$ NMR (377 MHz, $CDCl_3$) $\delta$ -66.49 (t, $J$ = 10.7 Hz, 3F), -116.98 ~ -117.02 (m, F). HRMS (EI) *m/z*: calcd for $C_{10}H_6NF_4Cl$ $[M-N_2]^+$ 251.0125, found: 251.0129.

**(*Z*)-1-Azido-1-(2-chlorophenyl)-4,4,4-trifluorobut-1-ene (3n).** Colorless oil; yield 68% (89 mg); $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 7.47 (d, $J$ = 8.0 Hz, 1H), 7.39 - 7.33 (m, 3H), 4.92 (t, $J$ = 7.2 Hz, 1H), 3.08 (qd, $J$ = 10.8, 7.2 Hz, 2H). $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) $\delta$ 140.1, 133.30, 133.2, 131.3, 131.0, 129.9, 127.2, 125.9 (q, $J$ = 279.2 Hz), 108.0 (q, $J$ = 3.5 Hz), 31.8 (q, $J$ = 30.7 Hz). $^{19}F$ NMR (377 MHz, $CDCl_3$) $\delta$-66.47 (t, $J$ = 10.8 Hz). HRMS (EI) *m/z*: calcd for $C_{10}H_7NF_3Cl$ $[M-N_2]^+$ 233.0219, found: 233.0211.

**(*Z*)-1-Azido-1-(2-chloro-4-fluorophenyl)-4,4,4-trifluorobut-1-ene (3o).** Colorless oil; yield 61% (85 mg). $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 7.39 - 7.34 (m, 1H), 7.32 - 7.30 (m, 1H), 7.11 (td, $J$ = 8.4, 1.1 Hz, 1H), 4.99 (t, $J$ = 7.2 Hz, 1H), 3.11 (qd, $J$ = 10.7, 7.2 Hz, 2H). $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) $\delta$ 160.4 (d, $J$ = 251.5 Hz), 135.0 (d, $J$ = 3.4 Hz), 132.7, 131.6 (d, $J$ = 9.4 Hz), 125.7 (q, $J$ = 276.7 Hz), 125.6 (d, $J$ = 3.6 Hz), 121.6 (d, $J$ = 19.7 Hz), 114.5 (d, $J$ = 22.4 Hz), 110.5 (q, $J$ = 3.4 Hz), 31.8 (q, $J$ = 30.9 Hz). $^{19}F$ NMR (377 MHz, $CDCl_3$) $\delta$ -66.43 (t, $J$ = 10.7 Hz, 3F), -110.63 ~ -110.66 (m, F). HRMS (EI) *m/z*: calcd for $C_{10}H_6NF_4Cl$ $[M-N_2]^+$ 251.0125, found: 251.0119.

**(*Z*)-1-Azido-1-(1-naphthaleneyl)-4,4,4-trifluorobut-1-ene (3p).** Colorless oil; yield

58% (65 mg). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.02 (d, $J$ = 8.3 Hz, 1H), 7.95 - 7.91 (m, 2H), 7.63 - 7.47 (m, 4H), 5.08 (t, $J$ = 7.3 Hz, 1H), 3.20 (qd, $J$ = 10.8, 7.3 Hz, 2H). $^{13}$C{$^1$H}NMR (100 MHz, $CDCl_3$) $\delta$ 141.3, 133.5, 131.9, 131.1, 130.1, 128.6, 127.5, 127.4, 126.5, 126.0 (q, $J$ = 275.6 Hz), 125.2, 124.5, 107.9 (q, $J$ = 3.5 Hz), 32.0 (q, $J$ = 30.5 Hz). $^{19}$F NMR (377 MHz, $CDCl_3$) $\delta$ -66.42 (t, $J$ = 10.8 Hz). HRMS (EI) *m/z*: calcd for $C_{14}H_{10}N_3F_3$ [$M^{+\cdot}$] 277.0827, found: 277.0831.

**(*Z*)-1-Azido-1-(3,4,5-trimethoxyphenyl)-4,4,4-trifluorobut-1-ene (3q).** Pale yellow oil; yield 86% (135 mg). $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 6.57 (s, 2H), 5.05 (t, $J$ = 7.2 Hz, 1H), 3.90 (s, 6H), 3.88 (s, 3H), 3.07 (qd, $J$ = 10.8, 7.2 Hz, 2H). $^{13}$C{$^1$H}NMR (100 MHz, $CDCl_3$) $\delta$ 153.4, 142.3, 139.1, 129.5, 125.9 (q, $J$ = 276.6 Hz), 106.2 (q, $J$ = 3.7 Hz), 104.5, 60.8, 56.1, 32.1 (q, $J$ = 30.5 Hz). $^{19}$F NMR (377 MHz, $CDCl_3$) $\delta$ -66.42 (t, $J$ = 10.8 Hz). HRMS (EI) *m/z*: calcd for $C_{13}H_{14}N_3O_3F_3$ [$M^{+\cdot}$] 317.0987, found: 317.0981.

**Typical experimental procedure for 4a**

Under Ar atmosphere, a solution of **1** (0.5 mmol), NuH (1.0 mmol), $Et_3N$ (15 mol%) and $KHCO_3$ (0.6 mmol) in dry DME (5 mL) was stirred at 65 ºC for 12 h. After the reaction was complete (monitored by TLC and GC analyses), the reaction was quenched with water. The aqueous layer was separated and extracted with EtOAc. The combined organic extracts were washed with brine, dried over $MgSO_4$, and solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel to afford the goal products.

**(*E*)-4,4,4-Trifluoro-1-phenylbut-2-en-1-ol (4aa).**[14] Colorless oil; yield 94% (94 mg).

$^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.43 - 7.37 (m, 3H), 7.33 - 7.31 (m, 2H), 6.55 - 6.49 (m, 1H), 6.06 - 5.97 (m, 1H), 5.25 - 5.23 (m, 1H), 2.72 (s, 1H). $^{13}$C{$^{1}$H}NMR (100 MHz, $CDCl_3$) $\delta$ 141.1 (q, $J$ = 6.1 Hz), 140.5, 129.0, 128.7, 126.6, 123.3 (q, $J$ = 269.3 Hz), 117.9 (q, $J$ = 34.1 Hz), 72.7. $^{19}$F NMR (377 MHz, $CDCl_3$) $\delta$ -64.38 (d, $J$ = 6.3 Hz).

**(*E*)-1,1,1-Trifluoro-4-methoxy-4-phenylbut-2-ene (4ab).** Colorless oil; yield 74% (80 mg). $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.44 - 7.32 (m, 5H), 6.50 - 6.45 (m, 1H), 6.04 (m, 1H), 4.79 - 4.76 (m, 1H), 3.35 (s, 3H). $^{13}$C{$^{1}$H}NMR (100 MHz, $CDCl_3$) $\delta$ 140.1 (q, $J$ = 6.3 Hz), 138.5, 128.8, 128.5, 127.2, 123.2 (q, $J$ = 269.4 Hz), 118.2 (q, $J$ = 34.0 Hz), 81.6, 56.7. $^{19}$F NMR (377 MHz, $CDCl_3$) $\delta$ -64.54 (d, $J$ = 6.3 Hz). HRMS (EI) *m/z*: calcd for $C_{11}H_{11}F_3O$ [$M^{+\cdot}$] 216.0762, found: 216.0754.

**(*E*)-4-Benzyloxy-1,1,1-trifluoro-4-phenylbut-2-ene (4ac).** Colorless oil; yield 80% (116 mg). $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.52 - 7.40 (m, 10H), 6.62 - 6.57 (m, 1H), 6.17 - 6.08 (m, 1H), 5.06 - 5.05 (m, 1H), 4.64 (d, $J$ = 11.9 Hz, 1H), 4.53 (d, $J$ = 11.9 Hz, 1H). $^{13}$C{$^{1}$H}NMR (100 MHz, $CDCl_3$) $\delta$ 140.3 (q, $J$ = 6.2 Hz), 138.6, 137.8, 129.0, 128.7, 128.6, 128.0, 127.8, 127.4, 123.3 (q, $J$ = 269.5 Hz), 118.2 (q, $J$ = 34.0 Hz), 79.0, 70.5. $^{19}$F NMR (377 MHz, $CDCl_3$) $\delta$ -64.47 (d, $J$ = 6.4 Hz). HRMS (APCI) *m/z*: calcd for $C_{17}H_{14}F_3O$ [M-H]$^{-}$ 291.1002, found: 291.1005.

**Transformations of 2a to 5a, 6a and 7a**

**Expermental procedure for 5a**

A mixture of **2a** (0.5 mmol), phenylacetylene (1.0 mmol), *L*-sodium ascorbate (10 mol%) and $CuSO_4 \cdot 5H_2O$ (1 mol%) in *t*-BuOH/$H_2O$ (2 mL, 1:1) was stirred at 25 ºC

for 12 h. After the reaction was complete (monitored by TLC and GC analyses), the reaction was quenched with water. The aqueous layer was separated and extracted with EtOAc. The combined organic extracts were washed with brine, dried over $MgSO_4$, and solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel to afford the white solid product.

**(*E*)-4-Phenyl-1-(4-phenyl-1,1,1-trifluorobut-3-en-2-yl)-*1H*-1.2.3-triazole (5a).** White solid, mp 166.5 - 166.7 ºC; yield 65% (107 mg). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.00 (s, 1H), 7.88 (d, $J$ = 6.9 Hz, 2H), 7.45 - 7.36 (m, 8H), 6.84 (d, $J$ = 15.7 Hz, 1H), 6.53 (dd, $J$ = 15.7, 7.7 Hz, 1H), 5.97 - 5.93 (m, 1H). $^{13}$C{$^1$H}NMR (100 MHz, $CDCl_3$) $\delta$ 148.7, 139.8, 134.4, 129.9, 129.6, 128.94, 128.89, 128.6, 127.1, 125.9, 123.0 (q, $J$ = 282.3 Hz), 118.8, 115.7, 63.9 (q, $J$ = 32.7 Hz). $^{19}$F NMR (377 MHz, $CDCl_3$) $\delta$ -74.05 (d, $J$ = 7.0 Hz). HRMS (ESI) *m/z*: calcd for $C_{18}H_{14}F_3N_3Na$ $[M+Na]^+$ 352.1038, found: 352.1036.

**Expermental procedure for 6a**

A mixture of **2a** (0.5 mmol) and 10% Pd/C (11.4 mg) in MeOH was stirred under $H_2$ atmosphere at 25 ºC for 12 h. After the reaction was complete (monitored by TLC and GC analyses), the reaction was filtered and the solvent was removed under reduced pressure to afforded goal product.

**1,1,1-Trifluoro-4-phenylbutan-2-amine (6a).** Colorless oil; yield 86% (87 mg). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.33 - 7.29 (m, 2H), 7.23 - 7.21 (m, 3H), 3.15 - 3.06 (m, 1H), 2.96 - 2.89 (m, 1H), 2.79 - 2.71 (m, 1H), 2.09 - 2.01 (m, 1H), 1.75 - 1.65 (m, 1H), 1.48 (s, 2H). $^{13}$C{$^1$H}NMR (100 MHz, $CDCl_3$) $\delta$140.9, 128.6, 128.5, 126.8 (q, $J$ =

281.6 Hz), 126.2, 53.0 (q, $J$ = 28.8 Hz), 31.6, 31.4 (q, $J$ = 1.3 Hz). $^{19}$F NMR (377 MHz, $CDCl_3$) $\delta$ -79.33 (d, $J$ = 7.3 Hz). HRMS (ESI) *m/z*: calcd for $C_{10}H_{13}F_3N$ $[M+H]^+$ 204.1000, found: 204.0990.

**Expermental procedure for 7a**

Under Ar atmosphere, a solution of **2a** (0.5 mmol), $PPh_3$ (0.75 mmol) and $H_2O$ (2.5 mmol) in THF (3 mL) was stirred at 25 ºC for 12 h. After the reaction was complete (monitored by TLC and GC analyses), the reaction was quenched with $NH_4Cl$ (aq.), extracted with $CH_2Cl_2$, dried over $MgSO_4$, and solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel to afford the goal product.

**(*E*)-1,1,1-Trifluoro-4-phenylbut-3-en-2-amine (7a).** Colorless oil; yield 68% (68 mg). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.45 - 7.28 (m, 5H), 6.83 (d, $J$ = 15.9 Hz, 1H), 6.20 (dd, $J$ = 15.9, 6.4 Hz, 1H), 4.04 - 3.97 (m, 1H), 1.62 (s, 2H). $^{13}$C{$^1$H}NMR (100 MHz, $CDCl_3$) $\delta$ 135.8, 134.7, 128.7, 128.4, 126.7, 125.8 (q, $J$ = 281.4 Hz), 122.4 (q, $J$ = 1.9 Hz), 55.9 (q, $J$ = 30.0 Hz). $^{19}$F NMR (377 MHz, $CDCl_3$) $\delta$ -78.35 (d, $J$ = 7.3 Hz). HRMS (ESI) *m/z*: calcd for $C_{10}H_{11}F_3N$ $[M+H]^+$ 202.0844, found: 202.0835.

**Transformations of 3 to 8**

A solution of **3** (0.2 mmol) in toluene (2 mL) was stirred at 110 ºC for 6 h - 12 h. After the reaction was complete (monitored by TLC), the solvent was removed under reduced pressure to afford goal product.

**2-(2,2,2-Trifluoroethyl)-3-phenyl-*2H*-azirine (8a).** Colorless oil; yield 92% (37 mg). $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.92 - 7.90 (m, 2H), 7.65 - 7.56 (m, 3H), 2.76 - 2.66

(m, 1H), 2.40 (dd, $J$ = 6.3, 4.8 Hz, 1H), 2.08 - 1.98 (m, 1H). $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) $\delta$ 168.9, 133.5, 129.7, 129.2, 126.3 (q, $J$ = 276.9 Hz), 124.3, 38.8 (q, $J$ = 28.3 Hz), 24.8 (q, $J$ = 4.4 Hz). $^{19}F$ NMR (377 MHz, $CDCl_3$) $\delta$ -65.49 (t, $J$ = 10.8 Hz). HRMS (EI) *m/z*: calcd for $C_{10}H_8NF_3$ [$M^{+\cdot}$] 199.0609, found: 199.0618.

**2-(2,2,2-Trifluoroethyl)-3-(4-methylphenyl)-*2H*-azirine (8b).** Colorless oil; yield 87% (37 mg). $^{1}H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.79 (d, $J$ = 8.1 Hz, 2H), 7.37 (d, $J$ = 8.1 Hz, 2H), 2.74 - 2.61 (m, 1H), 2.46 (s, 3H), 2.35 (dd, $J$ = 6.2, 4.8 Hz, 1H), 2.08 - 1.94 (m, 1H). $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) $\delta$ 168.4, 144.4, 130.0, 129.7, 126.4 (q, $J$ = 277.0 Hz), 121.5, 38.8 (q, $J$ = 28.2 Hz), 24.5 (q, $J$ = 4.4 Hz), 21.9. $^{19}F$ NMR (377 MHz, $CDCl_3$) $\delta$ -65.51 (t, $J$ = 10.9 Hz). HRMS (EI) *m/z*: calcd for $C_{11}H_{10}NF_3$ [$M^{+\cdot}$] 213.0765, found: 213.0773.

**2-(2,2,2-Trifluoroethyl)-3-(4-isopropylphenyl)-*2H*-azirine (8c).** Colorless oil; yield 99% (48 mg). $^{1}H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.85 (d, $J$ = 8.2 Hz, 2H), 7.44 (d, $J$ = 8.2 Hz, 2H), 3.05 - 2.98 (m, 1H), 2.75 - 2.62 (m, 1H), 2.37 (dd, $J$ = 6.2, 4.9 Hz, 1H), 2.10 - 1.96 (m, 1H), 1.31 (d, $J$ = 6.9 Hz, 6H). $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) $\delta$ 168.4, 155.2, 129.9, 127.4, 126.4 (q, $J$ = 276.9 Hz), 121.9, 38.9 (q, $J$ = 28.2 Hz), 34.5, 24.5 (q, $J$ = 4.4 Hz), 23.6. $^{19}F$ NMR (377 MHz, $CDCl_3$) $\delta$ -65.51 (t, $J$ = 10.9 Hz). HRMS (EI) *m/z*: calcd for $C_{13}H_{14}NF_3$ [$M^{+\cdot}$] 241.1078, found: 241.1083.

**2-(2,2,2-Trifluoroethyl)-3-(4-methoxyphenyl)-*2H*-azirine (8d).** Colorless oil; yield 98% (45 mg). $^{1}H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.83 (d, $J$ = 8.8 Hz, 2H), 7.05 (d, $J$ = 8.8 Hz, 2H), 3.89 (s, 3H), 2.75 - 2.61 (m, 1H), 2.33 (dd, $J$ = 6.3, 4.8 Hz, 1H), 2.05 - 1.92 (m, 1H). $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) $\delta$ 167.4, 163.7, 131.7, 126.4 (q, $J$ = 276.9

Hz), 116.8, 114.7, 55.5, 38.9 (q, $J$ = 28.1 Hz), 24.3 (q, $J$ = 4.4 Hz). $^{19}$F NMR (377 MHz, $CDCl_3$) $\delta$ -65.49 (t, $J$ = 10.9 Hz). HRMS (EI) *m/z*: calcd for $C_{11}H_{10}NOF_3$ [$M^{+\cdot}$] 229.0714, found: 229.0709.

**2-(2,2,2-Trifluoroethyl)-3-(4-fluorophenyl)-*2H*-azirine (8e).** Colorless oil; yield 96% (42 mg). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.96 - 7.92 (m, 2H), 7.31 - 7.26 (m, 2H), 2.83 - 2.69 (m, 1H), 2.41 (dd, $J$ = 6.4, 4.7 Hz, 1H), 2.07 - 1.94 (m, 1H). $^{13}$C{$^1$H}NMR (100 MHz, $CDCl_3$) $\delta$ 167.9, 165.8 (d, $J$ = 256.0 Hz), 132.1 (d, $J$ = 9.4 Hz), 126.3 (q, $J$ = 276.9 Hz), 120.7 (d, $J$ = 3.2 Hz), 116.7 (d, $J$ = 22.4 Hz), 38.8 (q, $J$ = 28.3 Hz), 24.9 (q, $J$ = 4.3 Hz). $^{19}$F NMR (377 MHz, $CDCl_3$) $\delta$ -65.50 (t, $J$ = 10.9 Hz, 3F), -104.03 ~ -104.10 (m, F). HRMS (EI) *m/z*: calcd for $C_{10}H_7NF_4$ [$M^{+\cdot}$] 217.0515, found: 217.0520.

**3-(4-Chlorophenyl)-2-(2,2,2-trifluoroethyl)-*2H*-azirine (8f).** Colorless oil; yield 94% (44 mg). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.83 (d, $J$ = 8.5 Hz, 2H), 7.54 (d, $J$ = 8.5 Hz, 2H), 2.80 - 2.67 (m, 1H), 2.40 (dd, $J$ = 6.3, 4.8 Hz, 1H), 2.05 - 1.92 (m, 1H). $^{13}$C{$^1$H}NMR (100 MHz, $CDCl_3$) $\delta$ 168.2, 139.9, 130.8, 129.7, 126.2 (q, $J$ = 276.9 Hz), 122.8, 38.7 (q, $J$ = 28.4 Hz), 25.0 (q, $J$ = 4.4 Hz). $^{19}$F NMR (377 MHz, $CDCl_3$) $\delta$ -65.49 (t, $J$ = 10.9 Hz). HRMS (EI) *m/z*: calcd for $C_{10}H_7NF_3Cl$ [$M^{+\cdot}$] 233.0219, found: 233.0222.

**3-(4-Bromophenyl)-2-(2,2,2-trifluoroethyl)-*2H*-azirine (8g).** Colorless oil; yield 88% (49 mg). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$7.76 (d, $J$ = 8.4 Hz, 2H), 7.71 (d, $J$ = 8.4 Hz, 2H), 2.80 - 2.67 (m, 1H), 2.40 (dd, $J$ = 6.2, 4.9 Hz, 1H), 2.05 - 1.91 (m, 1H). $^{13}$C{$^1$H}NMR (100 MHz, $CDCl_3$) $\delta$ 168.4, 132.7, 130.9, 128.5, 126.2 (q, $J$ = 276.9

Hz), 123.2, 38.7 (q, $J$ = 28.3 Hz), 25.1 (q, $J$ = 4.3 Hz). $^{19}$F NMR (377 MHz, $CDCl_3$) $\delta$ -65.47 (t, $J$ = 10.8 Hz). HRMS (EI) *m/z*: calcd for $C_{10}H_7NF_3Br$ [$M^{+\cdot}$] 276.9714, found: 276.9723.

**3-(4-Ethoxycarbonylphenyl)-2-(2,2,2-trifluoroethyl)-*2H*-azirine (8h).** Colorless oil; yield 100% (54 mg). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.21 (d, $J$ = 8.3 Hz, 2H), 7.95 (d, $J$ = 8.3 Hz, 2H), 4.41 (q, $J$ = 7.1 Hz, 2H), 2.78 - 2.66 (m, 1H), 2.44 (dd, $J$ = 6.1, 5.0 Hz, 1H), 2.09 - 1.96 (m, 1H), 1.41 (t, $J$ = 7.1 Hz, 3H). $^{13}$C{$^1$H}NMR (100 MHz, $CDCl_3$) $\delta$ 169.0, 165.4, 134.7, 130.3, 129.4, 127.8, 126.2 (q, $J$ = 276.9 Hz), 61.6, 38.6 (q, $J$ = 28.4 Hz), 25.3 (q, $J$ = 4.3 Hz), 14.2. $^{19}$F NMR (377 MHz, $CDCl_3$) $\delta$ -65.50 (t, $J$ = 10.8 Hz). HRMS (EI) *m/z*: calcd for $C_{13}H_{12}NO_2F_3$ [$M^{+\cdot}$] 271.0820, found: 271.0823.

**3-(4-Cyanophenyl)-2-(2,2,2-trifluoroethyl)-*2H*-azirine (8i).** Colorless oil; yield 92% (41 mg). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.01 (d, $J$ = 8.4 Hz, 2H), 7.86 (d, $J$ = 8.4 Hz, 2H), 2.85 - 2.72 (m, 1H), 2.48 (dd, $J$ = 6.3, 4.8 Hz, 1H), 2.07 - 1.93 (m, 1H). $^{13}$C{$^1$H}NMR (100 MHz, $CDCl_3$) $\delta$ 168.9, 133.0, 129.9, 128.1, 126.1 (q, $J$ = 276.9 Hz), 117.7, 116.8, 38.5 (q, $J$ = 28.5 Hz), 25.8 (q, $J$ = 4.3 Hz). $^{19}$F NMR (377 MHz, $CDCl_3$) $\delta$ -65.43 (t, $J$ = 10.8 Hz). HRMS (EI) *m/z*: calcd for $C_{11}H_7N_2F_3$ [$M^{+\cdot}$] 224.0561, found: 224.0566.

**3-[(1,1'-Biphenyl)-4-yl]-2-(2,2,2-trifluoroethyl)-*2H*-azirine (8j).** Colorless oil; yield 98% (54 mg). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.98 (d, $J$ = 8.3 Hz, 2H), 7.80 (d, $J$ = 8.3 Hz, 2H), 7.67 - 7.65 (m, 2H), 7.52 - 7.41 (m, 3H), 2.80 - 2.67 (m, 1H), 2.43 (dd, $J$ = 6.1, 4.9 Hz, 1H), 2.12 - 1.99 (m, 1H). $^{13}$C{$^1$H}NMR (100 MHz, $CDCl_3$) $\delta$ 168.5, 146.3, 139.7, 130.2, 129.1, 128.5, 127.9, 127.3, 126.4 (q, $J$ = 276.9 Hz), 123.0, 38.9

(q, $J$ = 28.2 Hz), 24.8 (q, $J$ = 4.3 Hz). $^{19}$F NMR (377 MHz, $CDCl_3$) $\delta$ -65.40 (t, $J$ = 10.8 Hz). HRMS (EI) *m/z*: calcd for $C_{16}H_{12}NF_3$ [$M^{+\cdot}$] 275.0922, found: 275.0932.

**2-(2,2,2-Trifluoroethyl)-3-(3-trifluoromethylphenyl)-*2H*-azirine (8k).** Colorless oil; yield 82% (44 mg). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.16 (s, 1H), 8.09 (d, $J$ = 7.7 Hz, 1H), 7.88 (d, $J$ = 7.9 Hz, 1H), 7.75 - 7.71 (m, 1H), 2.83 - 2.70 (m, 1H), 2.48 (dd, $J$ = 6.3, 4.8 Hz, 1H), 2.10 - 1.97 (m, 1H). $^{13}$C{$^1$H}NMR (100 MHz, $CDCl_3$) $\delta$ 168.8, 132.6, 132.1 (q, $J$ = 33.4 Hz), 129.97, 129.95 (q, $J$ = 3.1 Hz), 126.3 (q, $J$ = 3.8 Hz), 126.1 (q, $J$ = 281.7 Hz), 125.2, 123.4 (q, $J$ = 277.4 Hz), 38.6 (q, $J$ = 28.5 Hz), 25.5 (q, $J$ = 4.3 Hz). $^{19}$F NMR (377 MHz, $CDCl_3$) $\delta$ -63.55 (s, 3F), -65.52 (t, $J$ = 10.8 Hz, 3F). HRMS (EI) *m/z*: calcd for $C_{11}H_7NF_6$ [$M^{+\cdot}$] 267.0483, found: 267.0477.

**3-(3-Chlorophenyl)-2-(2,2,2-trifluoroethyl)-*2H*-azirine (8l).** Colorless oil; yield 99% (46 mg). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.87 (t, $J$ = 1.7 Hz, 1H), 7.78 (dt, $J$ = 7.5, 1.3 Hz, 1H), 7.60 - 7.57 (m, 1H), 7.53 - 7.49 (m, 1H), 2.78 - 2.64 (m, 1H), 2.42 (dd, $J$ = 6.2, 4.8 Hz, 1H), 2.09 - 1.95 (m, 1H). $^{13}$C{$^1$H}NMR (100 MHz, $CDCl_3$) $\delta$ 168.6, 135.4, 133.4, 130.6, 129.3, 127.7, 126.2 (q, $J$ = 276.9 Hz), 126.0, 38.6 (q, $J$ = 28.4 Hz), 25.3 (q, $J$ = 4.3 Hz). $^{19}$F NMR (377 MHz, $CDCl_3$) $\delta$ -65.48 (t, $J$ = 10.8 Hz). HRMS (EI) *m/z*: calcd for $C_{10}H_7NF_3Cl$ [$M^{+\cdot}$] 233.0219, found: 233.0221.

**3-(3-Chloro-2-fluorophenyl)-2-(2,2,2-trifluoroethyl)-*2H*-azirine (8m).** Colorless oil; yield 90% (45 mg). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.75 - 7.72 (m, 1H), 7.69 - 7.64 (m, 1H), 7.33 (m, 1H), 2.62 - 2.48 (m, 1H), 2.40 (t, $J$ = 5.3 Hz, 1H), 2.24 - 2.10 (m, 1H). $^{13}$C{$^1$H}NMR (100 MHz, $CDCl_3$) $\delta$ 165.0, 157.1 (d, $J$ = 262.5 Hz), 135.6, 129.2, 126.2 (q, $J$ = 277.0 Hz), 125.4 (d, $J$ = 4.9 Hz), 122.5 (d, $J$ = 16.3 Hz), 114.6 (d,

$J$ = 11.7 Hz), 38.5 (q, $J$ = 28.4 Hz), 24.1 (q, $J$ = 4.3 Hz). $^{19}$F NMR (377 MHz, $CDCl_3$) $\delta$ -65.45 (td, $J$ = 10.9, 1.9 Hz, 3F), -113.16 (br, F). HRMS (EI) *m/z*: calcd for $C_{10}H_6NF_4Cl$ [$M^{+\cdot}$] 251.0125, found: 251.0128.

**3-(2-Chlorophenyl)-2-(2,2,2-trifluoroethyl)-*2H*-azirine (8n).** Colorless oil; yield 100% (47 mg). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.87 - 7.85 (m, 1H), 7.56 - 7.51 (m, 1H), 7.48 - 7.44 (m, 1H), 2.42 - 2.30 (m, 3H). $^{13}$C{$^1$H}NMR (100 MHz, $CDCl_3$) $\delta$ 167.6, 136.1, 134.1, 132.1, 130.7, 127.4, 126.3 (q, $J$ = 277.2 Hz), 123.0, 38.7 (q, $J$ = 28.3 Hz), 25.0 (q, $J$ = 4.3 Hz). $^{19}$F NMR (377 MHz, $CDCl_3$) $\delta$ -65.35 (t, $J$ = 10.8 Hz). HRMS (EI) *m/z*: calcd for $C_{10}H_7NF_3Cl$ [$M^{+\cdot}$] 233.0219, found:233.0228.

**3-(2-Chloro-4-fluorophenyl)-2-(2,2,2-trifluoroethyl)-*2H*-azirine (8o).** Colorless oil; yield 99% (50 mg). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.53 (m, 1H), 7.37 (d, $J$ = 8.3 Hz, 1H), 7.18 (t, $J$ = 8.9 Hz, 1H), 2.60 - 2.48 (m, 1H), 2.37 (dd, $J$ = 6.8, 3.4 Hz, 1H), 2.17 - 2.03 (m, 1H). $^{13}$C{$^1$H}NMR (100 MHz, $CDCl_3$) $\delta$ 163.8, 162.3 (d, $J$ = 263.0 Hz), 136.8 (d, $J$ = 3.2 Hz), 135.1 (d, $J$ = 10.1 Hz), 126.5 (d, $J$ = 3.7 Hz), 126.3 (q, $J$ = 277.4 Hz), 115.0 (d, $J$ = 20.4 Hz), 112.7 (d, $J$ = 13.8 Hz), 38.7 (q, $J$ = 28.4 Hz), 24.0 (q, $J$ = 4.2 Hz). $^{19}$F NMR (377 MHz, $CDCl_3$) $\delta$ -65.37 (t, $J$ = 10.7 Hz, 3F), -108.21 (br, F). HRMS (EI) *m/z*: calcd for $C_{10}H_6NF_4Cl$ [$M^{+\cdot}$] 251.0125, found: 251.0126.

**2-(2,2,2-Trifluoroethyl)-3-(1-naphthaleneyl)-*2H*-azirine (8p).** Colorless oil; yield 98% (49 mg). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.98 (d, $J$ = 8.5 Hz, 1H), 8.09 (d, $J$ = 8.3 Hz, 1H), 7.97 - 7.94 (m, 2H), 7.74 - 7.70 (m, 1H), 7.66 - 7.61 (m, 2H), 2.75 - 2.61 (m, 1H), 2.40 - 2.38 (m, 1H), 2.26 - 2.13 (m, 1H). $^{13}$C{$^1$H}NMR (100 MHz, $CDCl_3$) $\delta$ 167.8, 134.2, 133.4, 132.8, 131.6, 128.64, 128.6, 127.2, 126.5 (q, $J$ = 277.1 Hz), 125.2,

125.1, 120.1, 38.8 (q, $J$ = 28.2 Hz), 21.5 (q, $J$ = 4.3 Hz). $^{19}$F NMR (377 MHz, $CDCl_3$) $\delta$ -65.27 (t, $J$ = 10.9 Hz). HRMS (EI) *m/z*: calcd for $C_{14}H_{10}NF_3$ [$M^{+\cdot}$] 249.0765, found: 249.0772.

**2-(2,2,2-Trifluoroethyl)-3-(3,4,5-trimethoxyphenyl)-*2H*-azirine (8q).** Pale yellow solid; mp 77.2 – 78.0 ºC; yield 100% (58 mg). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.11 (s, 2H), 3.92 (s, 3H), 3.90 (s, 6H), 2.79 - 2.66 (m, 1H), 2.37 (dd, $J$ = 6.6, 4.6 Hz, 1H), 2.03 - 1.89 (m, 1H). $^{13}$C{$^1$H}NMR (100 MHz, $CDCl_3$) $\delta$ 168.6, 153.8, 142.4, 126.3 (q, $J$ = 277.0 Hz), 119.2, 106.7, 61.0, 56.2, 38.8 (q, $J$ = 28.2 Hz), 25.2 (q, $J$ = 4.3 Hz). $^{19}$F NMR (377 MHz, $CDCl_3$) $\delta$ -65.44 (t, $J$ = 10.9 Hz). HRMS (EI) *m/z*: calcd for $C_{13}H_{14}NO_3F_3$ [$M^{+\cdot}$] 289.0926, found: 289.0934.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI:

Tables of the optimization of reaction conditions, X-ray structural information for **2q** and **3j**, and copies of $^1$H, $^{13}$C and $^{19}$F NMR spectra for products (PDF)

X-ray data for **2q** (CIF)

X-ray data for **3j** (CIF)

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**Notes**

The authors declare no competing financial interest.

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