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Synthesis of (*Z*)-*α*-Trifluoromethyl Alkenyl Triflate: a Scaffold for Diverse Trifluoromethylated Species

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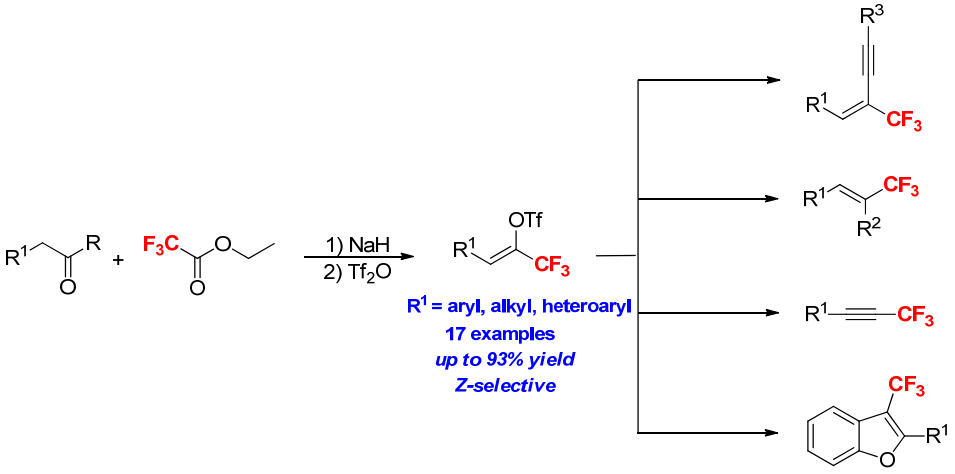


Abstract: An efficient method for the synthesis of (*Z*)-selective *α*-trifluoromethyl alkenyl triflates is described. As an important fluorinated building block, it is utilized successfully for the synthesis of various trifluoromethyl derivatives such as diarylethylenes, enynes, alkynes and benzofurans.

INTRODUCTION

It is generally known that introducing fluorine atoms into bioactive molecules can have some positive effects, such as rendering them more selective, potent, or increasing efficacy.[1] Among numerous fluorine-containing compounds, trifluoromethyl group constitutes an important structural motif of many biologically active compounds. Thus, an extensive variety of synthesis methodologies have been used to target trifluoromethyl-containing compounds.[2] In recent years, the trifluoromethylation catalyzed by transition-metals, such as silver,[3] copper including Cu(I)[4] and Cu(II),[5] nickel,[6] palladium,[7] platinum,[8] rhodium[9] *etc*. have been developed rapidly. Besides, a particularly promising approach for the synthesis of trifluoromethyl-containing compounds is through the use of appropriate trifluoromethylated building blocks. Avoiding the harsh reaction conditions and the use of toxic or expensive fluorinated reagents, trifluoromethylated building blocks have received much attention.[10]

Including C-C double bond and sulfonate ester unit, enol sulfonate ester is well known as an important organic synthesis intermediate because of easy derivatization.[11] Thus, introducing trifluoromethyl group to this framework would offer an effective fluorinated building block. However, only few countable reports on the synthesis and reactions of trifluoromethylated enol sulfonate esters with limited structures were available. The synthesis and applications of the enol sulfonate ester derived from ethyl trifluoroacetoacetate were disclosed by de Lera[12] and Lin.[13] Then, Shimizu and co-workers reported the synthesis and reactions of 1,1-dibromo-3,3,3-trifluoro-2-tosyloxypropene and 1,1-dichloro-3,3,3-trifluoro-2-tosyloxy-propene.[14] Also,

photoredox-catalyzed stereoselective trifluoromethyl-triflation of alkynes afforded (*E*)-*β*-trifluoromethyl alkenyl triflates.[15] Herein, a general method to prepare trifluoromethylated enol sulfonate esters with various functional groups has yet to be developed. In view of the high geometrical specificity of C-C double bond units present in many biologically active compounds, geometrically selective synthesis of trifluoromethylated enol sulfonate ester, especially with *Z*-selectivity, is still highly desirable.

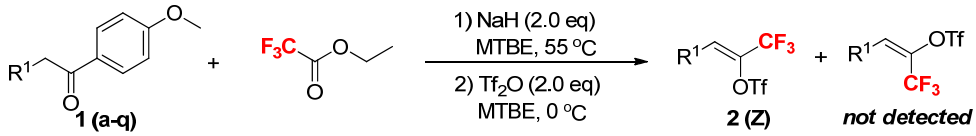
Recently, our group reported an efficient method for the preparation of trifluoromethyl ketones via the reaction between alkyl aryl ketones and ethyl trifluoroacetate.[16] In that transformation, a C-C bond cleavage step was witnessed, and trifluoromethylated enol anion was generated in the reaction mixture. The trifluoromethylated enol anion was successfully captured as (*Z*)-*α*-trifluoromethyl alkenyl triflates when Tf_2O was added to the reaction mixture upon the consumption of the substrate. This procedure represents an operationally simple, highly efficient method for the synthesis of (*Z*)-*α*-trifluoromethyl alkenyl triflates. Herein, we present the synthesis of (*Z*)-*α*-trifluoromethyl alkenyl triflates and their applications in the straightforward synthesis of trifluoromethylated alkenes, alkynes, enynes and benzofurans.

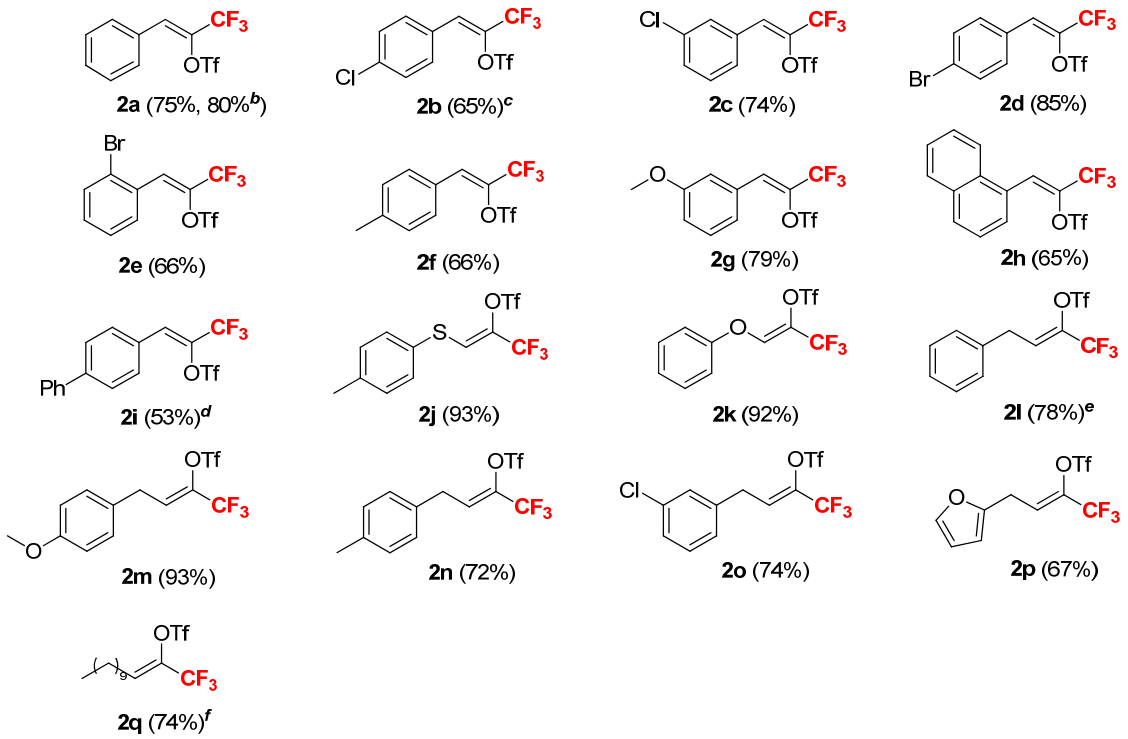
RESULTS AND DISCUSSION

As an extension of our previous study, *α*-trifluoromethyl substituted alkenyl triflates

(**2**) were synthesized in good yields from alkyl aryl ketones (**1**), ethyl trifluoroacetate and triflic anhydride (Table 1). The alkyl aryl ketones and ethyl trifluoroacetate undergo the "trifluoroacetic ester/ketone metathesis" to form the trifluoromethylated enol anions, which were captured by triflic anhydride in the second step to generate α-trifluoromethyl substituted alkenyl triflates. Different with our previous study,[16] methyl tert-butyl ether (MTBE) was used as reaction solvent instead of THF only because THF can be easily transferred into the ring-opening polymerization byproduct when triflic anhydride was used in the second step. To our surprise, ^{1}H NMR of the crude product showed that a single isomer was formed. Further, a single-crystal of **2e** was prepared, and its structure was confirmed to be *Z* by X-ray single-crystal diffraction, as shown in Figure S1 (see SI).

Table 1. *Z*-Selective Synthesis of Trifluoromethylated Alkenyl Triflates[a]





[a]Reaction conditions: **1** (5 mmol), CF_3COOEt (10 mmol), NaH (10 mmol), MTBE (10 mL) at 55 °C for 6 - 12 h under Ar atmosphere and then drop Tf_2O (10 mmol) at 0 °C for 5 - 10 min. [b]The yield was determined by ^{19}F NMR with *m*-$BrC_6H_4CF_3$ as an internal standard. [c]The reaction was conducted on a 30.5 mmol scale with CF_3COOEt (10 mL) and NaH (61 mmol) in MTBE (200 mL) and then Tf_2O (6.5 mL). [d]The reaction was conducted on a 1 mmol scale with CF_3COOEt (2 mmol) and NaH (2 mmol) in MTBE (5 mL) and then Tf_2O (2 mmol) in CH_2Cl_2 (5 mL). [e]The reaction was conducted on a 2.0 mmol scale 1-(3,4-dimethoxyphenyl)-3-phenylpropan-1-one with CF_3COOEt (6.0 mmol) and NaH (4.0 mmol) in MTBE (10 mL) and then Tf_2O (6.0 mmol). [f]The reaction was conducted on a 2.0 mmol scale 1-phenyldodecan-1-one with CF_3COOEt (8.0 mmol) and NaH (4.0 mmol) in MTBE (10 mL) and then Tf_2O (6.0 mmol).

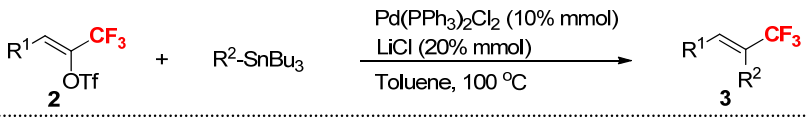
Encouraged by the results obtained, the scope in terms of ketones was explored (Table 1). Various enolizable phenyl ketones bearing either electron-withdrawing or –donating groups were converted smoothly to the corresponding alkenyl triflates. The ketone substrates with functional groups such as phenyl, chloro, alkoxy, bromo, and heterocycles *etc.* gave the desired products in moderate to excellent yields. Electronic effect has little impact on the reaction. The ketone substrates with either electron-withdrawing or –donating groups in the same position (**2b**, **2f**; **2c**, **2g**) have the similar results. Nonetheless, a slightly lower yield was observed with *ortho*-substituents (**2e**) compared with *para*-substituents (**2d**). That is likely due to the steric hindrance. Furthermore, the relatively low yield of **2i** was attributed to the poor solubility of the corresponding ketone (**1i**) in MTBE. The heteroaryl substrate **1p** was converted effectively into alkenyl triflate **2p** in 67% yield as well as the ketones containing *β*-oxygen or *β*-sulphur atom in 92% and 93% yield, respectively. Moreover, the substrate with linear aliphatic chain (**1q**) gave the desired alkenyl triflate **2q** in good yield. Similar with **2e**, excellent *Z*-selectivity was confirmed by ^{1}H NMR of the crude products for all the substances.

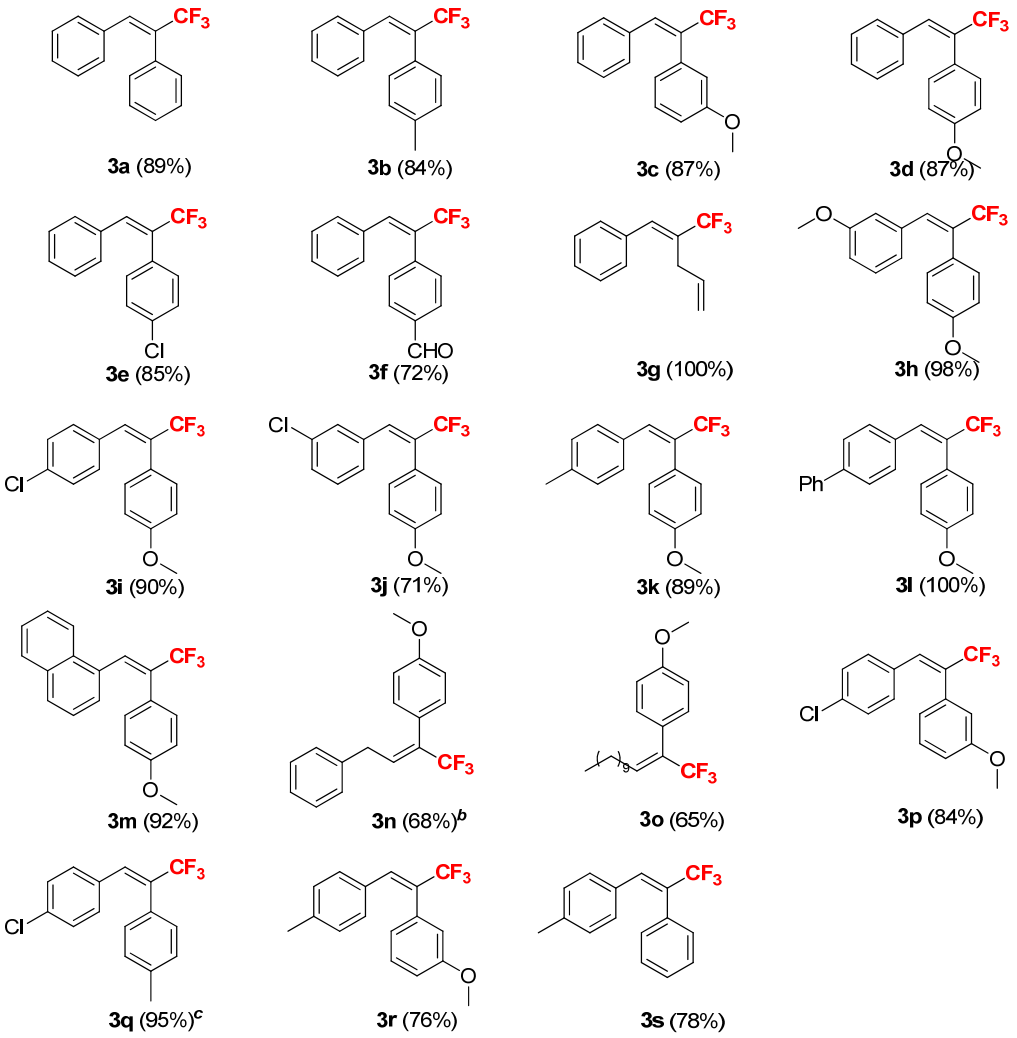
Bearing easily derived C-C double bond and sulfonate ester unit, trifluoromethylated alkenyl triflates can be used for the synthesis of various trifluoromethyl derivatives, such as diarylethylenes,[17] enynes,[18] alkynes[19] and benzofurans.[20]

Thus, the cross-coupling reactions of trifluoromethylated alkenyl triflates with aryl

metal reagents to afford trifluoromethylated diarylethylenes were preferentially explored. Great challenge encountered by PhZnCl was the generation of the undesired homocoupling byproduct, biphenyl, which is difficult to separate from the product, trifluoromethylated diarylethylene (**3**). Fortunately, without any homocoupling byproduct, introduction of an aryl or alkane group was accomplished with aryl-$SnBu_3$ or alkyl-$SnBu_3$. Under the general condition of Stille coupling,[21] trifluoromethylated alkenyl triflates were converted into trifluoromethylated diarylethylenes with retention of the configuration of C-C double bond (Table 2). Both trifluoromethylated alkenyl triflates and tributyl aryl tins with electron-withdrawing or –donating groups worked well, giving the desired trifluoromethylated diarylethylenes in good to excellent yields. Unfortunately, the *ortho*-substituted $ArSnBu_3$ was much less reactive under this condition as a result of steric hindrance. The substrate with linear aliphatic chain reacted well to afford corresponding product **3o**. In all of the cases, ^1H NMR of the crude products showed only one isomer of the C-C double bond was formed. The absolute configuration of **3q** was determined to be *E*-configured double bond by X-ray single-crystal diffraction, as shown in Figure S2 (see SI).

Table 2. Stille Coupling Reactions of Alkenyl Triflates[a]



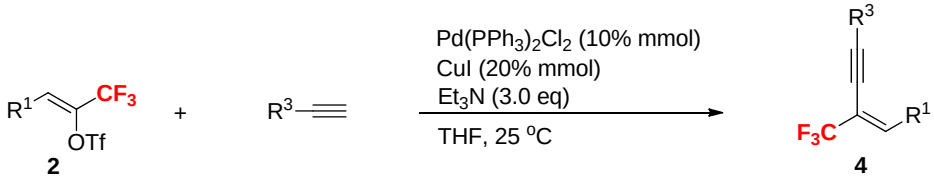


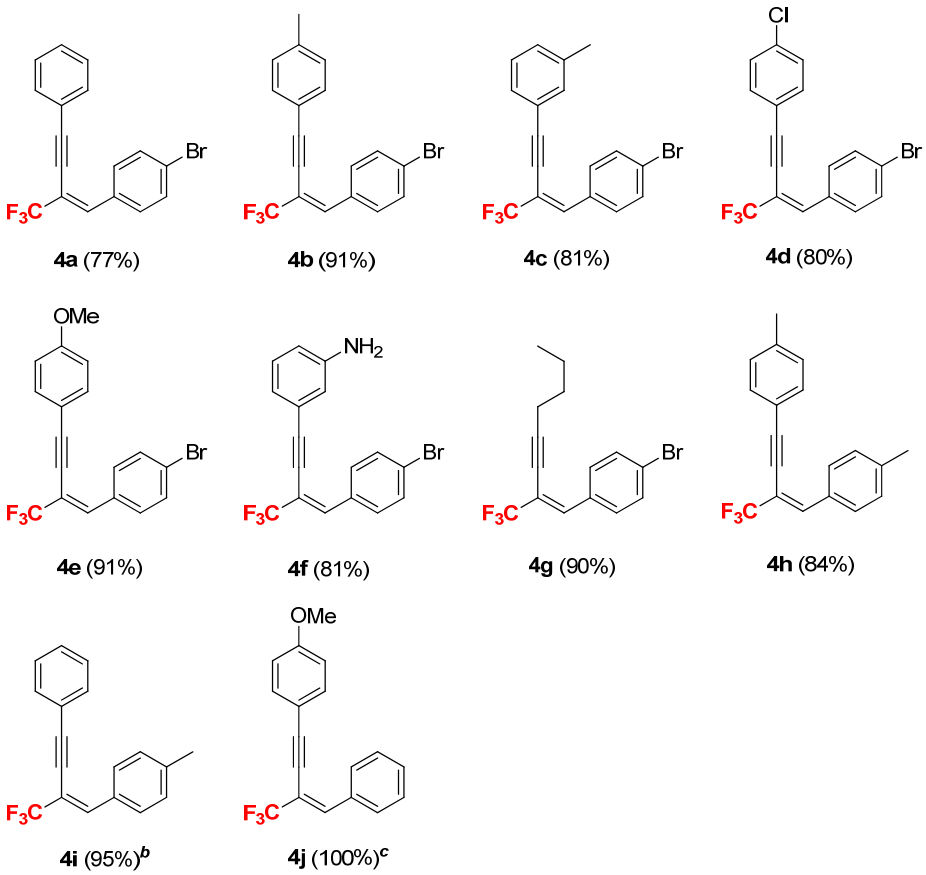
[a]Reaction conditions: **2** (0.5 mmol), tributyl tin compounds (0.75 mmol), $Pd(PPh_3)_2Cl_2$ (10% mmol), LiCl (20% mmol), toluene (3 mL) at 100 °C for 6-12 h under Ar atmosphere. [b]The reaction was conducted on a 3.0 mmol scale with (p-CH_3O)$C_6H_4SnBu_3$ (4.5 mmol), $Pd(PPh_3)_2Cl_2$ (10% mmol), LiCl (20% mmol) in toluene (10 mL). [c]The reaction was conducted on a 2.8 mmol scale with (p-CH_3)$C_6H_4SnBu_3$ (4.2 mmol), $Pd(PPh_3)_2Cl_2$ (10% mmol), LiCl (20% mmol) in toluene (15 mL).

The trifluoromethylated enynes are important building blocks for functionalized

trifluoromethylated compounds.[22] Herein, successful Sonogashira coupling[23] of trifluoromethylated alkenyl triflates with alkynes was also established to afford trifluoromethylated enynes (Table 3). (*Z*)-1-(4-bromophenyl)-3,3,3-trifluoroprop-1-en-2-yl trifluoromethanesulfonate was investigated to react with diverse alkynes in most cases. Remarkably, good regioselectivity between triflate and bromo was achieved. Thus, trifluoromethylated enynes with methyl, chloro, methoxy and even amino were obtained in good to excellent yields. In addition, alkyl-substituted alkyne was transformed into corresponding enyne smoothly in 90% yield (**4g**).

Table 3. Sonogashira Coupling Reaction of Alkenyl Triflates[a]



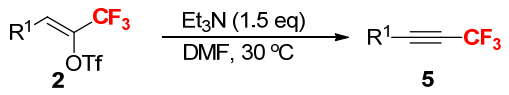


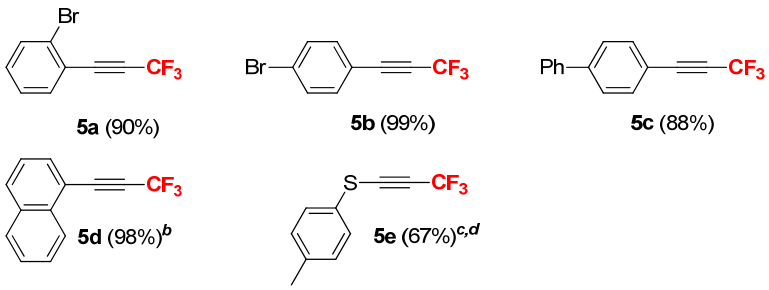
[a]Reaction conditions: **2** (1.25 mmol or 2.5 mmol), alkyne (1.1 eq), $Pd(PPh_3)_2Cl_2$ (10% mmol), CuI (20% mmol), Et_3N (3.0 eq), THF (5 mL) at 25 °C for 12 h under Ar atmosphere. [b]The reaction was conducted on a 0.51 mmol scale with alkyne (1.2 eq), $Pd(PPh_3)_2Cl_2$ (10% mmol), CuI (20% mmol), Et_3N (2.0 eq) in THF (3 mL). [c]The reaction was conducted on a 0.5 mmol scale with alkyne (1.1 eq), $Pd(PPh_3)_2Cl_2$ (10% mmol), CuI (20% mmol) in Et_3N (3 mL).

Also, as versatile building blocks have received much attention, trifluoromethylated alkynes have found widespread use in medicinal, agrochemical, and material science.[24] Therefore, synthesis of trifluoromethylated alkynes *via* elimination reaction of

trifluoromethylated alkenyl triflates is put on our schedule. Trifluoromethylated alkenyl triflate **2d** was explored as the model substrate firstly. Preliminary results, using LC analysis with biphenyl as an internal standard, indicated that polar aprotic solvents such as DMF, DMSO, NMP gave the desire product in excellent yield with the promotion of weak bases such as Et_3N, $NaHCO_3$ or $KHCO_3$ under mild condition. The solvents, such as THF, Et_2O, toluene *etc.* were proved to be less effective even totally ineffective unless the reactions were carried out at high temperature. In addition, the hydrolysis product, trifluoromethyl ketone, was formed if the solvent was not sufficiently dried. With the optimal conditions in hand, several substrates were investigated. As depicted in Table 4, trifluoromethylated alkenyl triflates furnished trifluoromethylated alkynes in excellent yields. Slightly lower yield of **5e** is likely due to its chemical instability.

Table 4. Elimination Reaction of Alkenyl Triflates[a]



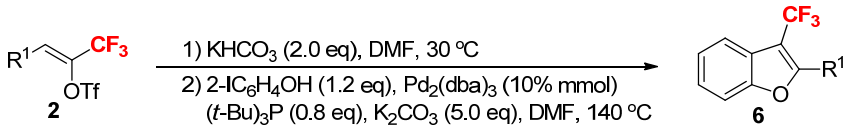


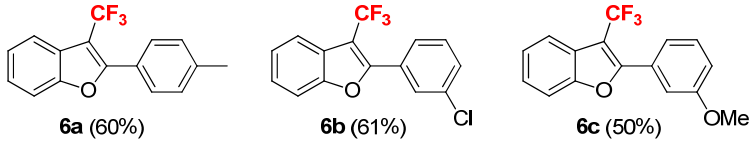
[a]Reaction conditions: **2** (1.3 mmol), Et_3N (1.5 eq), DMF (3 mL) at 30 °C for 12 h. [b]The reaction was conducted on a 0.51 mmol scale with Et_3N (1.5 eq) in DMF (2 mL). [c]The reaction was conducted on a 1 mmol scale with Et_3N (2.0 eq) in DMF (5 mL). [d]Labile

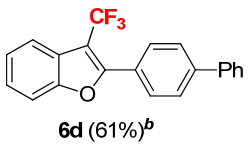
compound.

Furthermore, using **2** and 2-iodophenol with the $Pd(OAc)_2$/X-Phos/Cs_2CO_3 catalyst system, we tried the synthesis of 3-trifluoromethylbenzofuran, an essential structural motifs in biologically active compounds.[25] After intensive investigation, as depicted in Table 5, a series of 3-trifluoromethylbenzofuran compounds were obtained in moderate yield in one-pot by two steps. According to the reported mechanism of similar transformation,[20e] the elimination of **2** affords 1-aryltrifluoropropynes firstly, followed by Michael-type addition with 2-iodophenol at 1-position of 1-aryltrifluoropropynes, then the formed vinyl ether intermediates were transferred to the desired products, 3-trifluoromethylbenzofurans (**6**), *via* intramolecular Heck cross-coupling reaction.

Table 5. Synthesis of 3-Trifluoromethylbenzofurans[a]



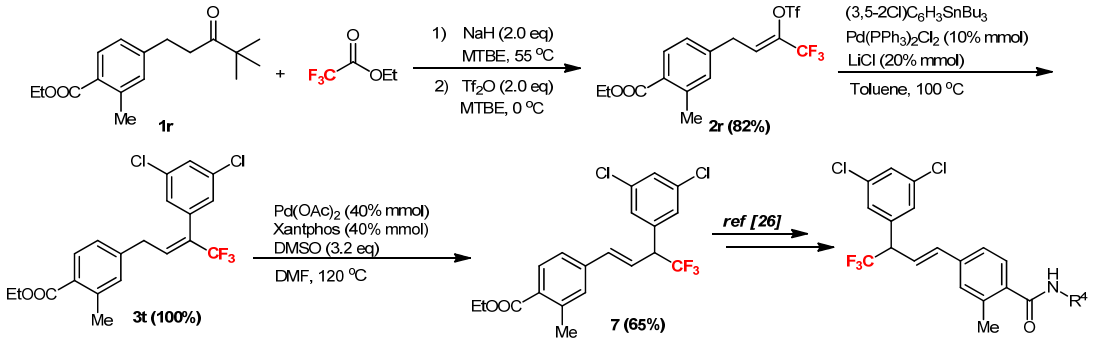




[a]Reaction conditions: **2** (0.5 mmol), $KHCO_3$ (2.0 eq), DMF (5 mL), 30 °C for 12 h and then 2-IC_6H_4OH (1.2 eq), $Pd_2(dba)_3$ (10% mmol), (*t*-Bu)$_3$P (0.8 eq), K_2CO_3 (5.0 eq) were added *in situ* under Ar, at 140 °C for 12 h. [b]24 h.

Finally, as mentioned above, the trifluoromethylated alkenyl triflates are extremely useful precursors and can be used to synthesize a series of bioactive molecules. As shown in Scheme 1, an intermediate for a new type of pesticides[26] was prepared according to our method. **2r** was obtained from ketone **1r** with ethyl trifluoroacetate, and then transfer to **3t** quantitatively *via* the Stille coupling. Under the catalysis of $Pd(OAc)_2$-Xantphos-DMSO in DMF, **3t** isomerized to generate **7**, from which a series of compounds with high pesticidal activity can be easily prepared.

Scheme 1. Synthesis of the intermediate for pesticides



In summary, using ethyl trifluoroacetate as a trifluoromethylation reagent, we developed an efficient method to afford (*Z*)-*α*-trifluoromethyl alkenyl triflates with excellent stereoselectivity *via* trifluoroacetic ester/ketone exchange process. Bearing the biologically important CF_3-moiety, easily derived C-C double bond and sulfonate ester unit, trifluoromethylated alkenyl triflates are important scaffolds, from which diverse trifluoromethyl derivatives, such as diarylethylenes, enynes, alkynes and benzofurans, were easily prepared *via* Stille coupling, Sonogashira coupling, elimination and

cyclization reactions, respectively. Further studies on the other application of (*Z*)-trifluoromethyl alkenyl triflates are currently underway in our laboratory.

EXPERIMENTAL SECTION

General method. Unless otherwise noted, all reactions were performed under Ar atmosphere in oven-dried glassware with magnetic stirring. Anhydrous solvents were freshly distilled from sodium and benzophenone or calcium hydride. 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 ($^{13}C\{H\}$), and 377 MHz or 470 MHz (^{19}F) on a spectrometer. Chemical shift (δ) were reported in parts per million (ppm) relative to the residual solvent signal. HRMS (EI) 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. The enolizable ketones were purchased from commercial sources or prepared from corresponding acetophenone and aldehydes, reduced by Pd/C-catalyzed hydrogenation according to the literature[27] or prepared from corresponding phenylacetic acid and anisole.[28]

General procedure for the preparation of trifluoromethylated alkenyl triflates (2).

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 enolizable ketone (5.0 mmol) in MTBE (5 mL) was

added, and the mixture was refluxed for 6-12 h. After reaction completed (monitored by TLC and GC analysis), the reaction solution was cooled to 0 °C. Tf_2O (2.82 g, 10 mmol) was added dropwise to the reaction mixture. After reaction completion (monitored by TLC and GC analysis), 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.

(*Z*)-1-Phenyl-3,3,3-trifluoroprop-1-en-2-yl trifluoromethanesulfonate (2a). Colorless oil; yield 75% (1.2 g); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 - 7.58 (m, 2H), 7.47 - 7.45 (m, 3H), 7.13 (s, 1H). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 132.4 (q, J = 38.3 Hz), 131.1, 129.9, 129.1, 128.6, 128.1 (q, J = 3.5 Hz), 119.2 (q, J = 271.0 Hz), 118.3 (q, J = 319.1 Hz). ^{19}F NMR (470 MHz, $CDCl_3$) δ -69.18 (q, J = 5.7 Hz, 3F); -72.99 (q, J = 5.7 Hz, 3F). HRMS (EI) *m/z*: calcd for $C_{10}H_6F_6O_3S$ [$M^{+\cdot}$] 319.9942, found: 319.9944.

(*Z*)-1-(4-Chlorophenyl)-3,3,3-trifluoroprop-1-en-2-yl trifluoromethanesulfonate (2b). Colorless oil; yield 65% (7.03 g); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 8.8 Hz, 2H), 7.44 (d, J = 8.8 Hz, 2H), 7.08 (s, 1H). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 137.4, 132.8 (q, J = 38.5 Hz), 131.1, 129.5, 127.0, 126.9 (q, J = 4.0 Hz), 119.1 (q, J = 271.2 Hz), 118.3 (q, J = 319.4 Hz). ^{19}F NMR (470 MHz, $CDCl_3$) δ -69.17 (q, J = 5.8 Hz, 3F); -72.69 (q, J = 5.8 Hz, 3F). HRMS (EI) *m/z*: calcd for $C_{10}H_5ClF_6O_3S$ [$M^{+\cdot}$] 353.9552, found: 353.9561.

(*Z*)-1-(3-Chlorophenyl)-3,3,3-trifluoroprop-1-en-2-yl trifluoromethanesulfonate (2c).

Corlorless oil; yield 74% (1.3 g); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (s, 1H), 7.36-7.47 (m, 3H), 7.08 (s, 1H). $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ 135.2, 133.4 (q, J = 38.8 Hz), 131.1, 130.4, 130.2, 129.7, 127.8, 126.7 (q, J = 3.6 Hz), 119.0 (q, J = 280.8 Hz), 118.3 (q, J = 318.6 Hz). ^{19}F NMR (470 MHz, $CDCl_3$) δ -69.43 (q, J = 6.0 Hz, 3F); -72.88 (q, J = 6.0 Hz, 3F). HRMS (EI) *m/z*: calcd for $C_{10}H_5ClF_6O_3S$ [$M^{+\cdot}$] 353.9552, found: 353.9553.

(*Z*)-1-(4-Bromophenyl)-3,3,3-trifluoroprop-1-en-2-yl trifluoromethanesulfonate (2d). Colorless oil; yield 85% (1.7 g); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 (s, 1H), 7.47 (d, J = 8.8 Hz, 2H), 7.61 (d, J = 8.8 Hz, 2H). $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ 132.8 (q, J = 30.9 Hz), 132.5, 131.2, 127.4, 127.0 (q, J = 2.8 Hz), 125.7, 119.1 (q, J = 217.0 Hz), 118.3 (q, J = 255.5 Hz). ^{19}F NMR (470 MHz, $CDCl_3$) δ -69.24 (q, J = 6.2 Hz, 3F); -72.74 (q, J = 6.2 Hz, 3F). HRMS (EI) *m/z*: calcd for $C_{10}H_5BrF_6O_3S$ [$M^{+\cdot}$] 397.9047, found: 397.9044.

(*Z*)-1-(2-Bromophenyl)-3,3,3-trifluoroprop-1-en-2-yl trifluoromethanesulfonate (2e). White solid; yield 66% (1.31 g); mp 34.0 °C - 34.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 8.0 Hz, 1H), 7.61 (d, J = 7.7 Hz, 1H), 7.41 (m, 1H), 7.37 (s, 1H), 7.32 (m, 1H). $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ 134.2 (q, J = 39.0 Hz), 133.2, 131.9, 130.6, 129.4, 127.8, 127.4 (q, J = 3.7 Hz), 124.3, 118.9 (q, J = 217.1 Hz), 118.2 (q, J = 255.3 Hz). ^{19}F NMR (470 MHz, $CDCl_3$) δ -69.77 ~ -69.72 (m, 3F); -73.22 ~ -73.17 (m, 3F). HRMS (EI) *m/z*: calcd for $C_{10}H_5BrF_6O_3S$ [$M^{+\cdot}$] 397.9047, found: 397.9058.

(*Z*)-1-(4-Methylphenyl)-3,3,3-trifluoroprop-1-en-2-yl trifluoromethanesulfonate (2f). Colorless oil; yield 66% (1.1 g); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, J = 8.2 Hz, 2H),

7.26 (d, J = 8.2 Hz, 2H), 7.08 (s, 1H), 2.40 (s, 3H). $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ 141.8, 131.6 (q, J = 38.6 Hz), 130.0, 129.9, 128.1 (q, J = 3.6 Hz), 125.7, 119.4 (q, J = 270.8 Hz), 118.4 (q, J = 319.2 Hz), 21.4. ^{19}F NMR (470 MHz, $CDCl_3$) δ -68.97 (q, J = 6.2 Hz, 3F); -72.94 (q, J = 6.2 Hz, 3F). HRMS (EI) *m/z*: calcd for $C_{11}H_8F_6O_3S$ [$M^{+\cdot}$] 334.0098, found: 334.0104.

(*Z*)-1-(3-Methoxyphenyl)-3,3,3-trifluoroprop-1-en-2-yl trifluoromethanesulfonate (2g). Colorless oil; yield 79% (1.37 g); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (t, J = 8.0 Hz, 1H), 7.21 (d, J = 1.1 Hz, 1H), 7.14 (m, 2H), 7.03 (dd, J = 8.0, 2.4 Hz, 1H), 3.85 (s, 3H). $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ 160.0, 132.4 (q, J = 38.5 Hz), 130.1, 129.7, 128.1 (q, J = 3.6 Hz), 122.7, 119.2 (q, J = 270.9 Hz), 118.3 (q, J = 319.2 Hz), 117.7, 114.1, 55.2. ^{19}F NMR (470 MHz, $CDCl_3$) δ -69.31 ~ -69.27 (m, 3F); -73.03 ~ -72.99 (m, 3F). HRMS (EI) *m/z*: calcd for $C_{11}H_8F_6O_4S$ [$M^{+\cdot}$] 350.0048, found: 350.0049.

(*Z*)-1-(Naphthalen-1-yl)-3,3,3-trifluoroprop-1-en-2-yl trifluoromethanesulfonate (2h). White solid; yield 65% (1.2 g); mp 53.5 °C - 53.7 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, J = 8.3 Hz, 1H), 7.85 (m, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.70 (s, 1H), 7.66 (d, J = 7.1 Hz, 1H), 7.51 (m, 3H). $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ 134.6 (q, J = 38.7 Hz), 133.5, 131.2, 131.1, 128.9, 127.9, 127.4, 126.7, 126.6 (dd, J = 6.8 Hz, 3.3 Hz), 119.2 (q, J = 217.0 Hz), 118.2 (q, J = 255.2 Hz). ^{19}F NMR (470 MHz, $CDCl_3$) δ -69.53 ~ -69.50 (m, 3F); -73.48 ~ -73.43 (m, 3F). HRMS (EI) *m/z*: calcd for $C_{14}H_8F_6O_3S$ [$M^{+\cdot}$] 370.0098, found: 370.0099.

(*Z*)-1-([1,1'-Biphenyl]-4-yl)-3,3,3-trifluoroprop-1-en-2-yl trifluoromethanesulfonate

(2i). White solid; yield 53% (210 mg); mp 79.7 °C - 80.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (s, 4H), 7.64 (d, J = 7.6 Hz, 2H), 7.49 (t, J = 7.5 Hz, 2H), 7.41 (t, J = 7.3 Hz, 1H), 7.17 (s, 1H). ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 143.9, 139.6, 132.1 (q, J = 38.6 Hz), 130.5, 129.0, 128.2, 127.8 (q, J = 3.5 Hz), 127.7, 127.3, 127.2, 119.3 (q, J = 271.1 Hz), 118.3 (q, J = 319.4 Hz). ^{19}F NMR (470 MHz, $CDCl_3$) δ -68.83 (q, J = 5.9 Hz, 3F); -72.65 (q, J = 5.9 Hz, 3F). HRMS (EI) *m/z*: calcd for $C_{16}H_{10}F_6O_3S$ [$M^{+\cdot}$] 396.0255, found: 396.0258.

(*Z*)-1-(*p*-Tolylthio)-3,3,3-trifluoroprop-1-en-2-yl trifluoromethanesulfonate (2j). Colorless oil; yield 93% (1.69 g); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, J = 8.1 Hz, 2H), 7.22 (d, J = 8.1 Hz, 2H), 7.17 (s, 1H), 2.38 (s, 3H). ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 140.1, 133.8 (q, J = 3.4 Hz), 132.1, 130.6, 128.5 (q, J = 40.7 Hz), 127.1, 118.6 (q, J = 231.5 Hz), 118.4 (q, J = 239.7 Hz), 21.0. ^{19}F NMR (470 MHz, $CDCl_3$) δ -68.56 (q, J = 4.2 Hz, 3F); -72.95 (q, J = 4.2 Hz, 3F). HRMS (EI) *m/z*: calcd for $C_{11}H_8F_6O_3S_2$ [$M^{+\cdot}$] 365.9819, found: 365.9824.

(*Z*)-1-Phenoxy-3,3,3-trifluoroprop-1-en-2-yl trifluoromethanesulfonate (2k). Colorless oil; yield 92% (1.54 g); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (m, 3H), 7.21 (t, J = 7.4 Hz, 1H), 7.07 (d, J = 8.2 Hz, 2H). ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 155.8, 142.3 (q, J = 4.5 Hz), 130.2, 125.8, 121.8 (q, J = 40.1 Hz), 119.9 (q, J = 214.6 Hz), 118.6 (q, J = 254.9 Hz), 117.2. ^{19}F NMR (470 MHz, $CDCl_3$) δ -68.90 (q, J = 3.5 Hz, 3F); -73.32 (q, J = 3.5 Hz, 3F). HRMS (EI) *m/z*: calcd for $C_{10}H_6F_6O_4S$ [$M^{+\cdot}$] 335.9891, found: 335.9883.

(*Z*)-4-Phenyl-1,1,1-trifluorobut-2-en-2-yl trifluoromethanesulfonate (2l). Colorless oil;

yield 78% (520 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.19 (m, 5H), 6.49 (t, J = 7.6 Hz, 1H), 3.68 (d, J = 7.5 Hz, 2H). $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ 135.7, 134.0 (q, J = 39.4 Hz), 130.0 (q, J = 3.2 Hz), 129.1, 128.5, 127.5, 118.7 (q, J = 289.7 Hz), 118.4 (q, J = 299.6 Hz), 32.1. ^{19}F NMR (470 MHz, $CDCl_3$) δ -69.95 ~ -69.91 (m, 3F); -72.90 ~ -72.86 (m, 3F). HRMS (EI) *m/z*: calcd for $C_{11}H_8F_6O_3S$ [$M^{+\cdot}$] 334.0098, found: 334.0107.

(*Z*)-4-(4-Methoxyphenyl)-1,1,1-trifluorobut-2-en-2-yl trifluoromethanesulfonate (2m). Colorless oil; yield 93% (1.68 g); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (d, J = 8.6 Hz, 2H), 6.88 (d, J = 8.6 Hz, 2H), 6.47 (t, J = 7.6 Hz, 1H), 3.80 (s, 3H), 3.62 (dd, J = 7.6, 1.6 Hz, 2H). $^{13}C\{^{1}H\}$NMR (100 Hz, $CDCl_3$) δ 159.0, 133.6 (q, J = 39.3 Hz), 129.6, 127.6, 118.7 (q, J = 288.2 Hz), 118.5 (q, J = 300.9 Hz), 114.4, 55.2, 31.3. ^{19}F NMR (470 MHz, $CDCl_3$) δ -70.01 (q, J = 4.4 Hz, 3F); -73.07 (q, J = 4.4 Hz, 3F). HRMS (EI) *m/z*: calcd for $C_{12}H_{10}F_6O_4S$ [$M^{+\cdot}$] 364.0204, found: 364.0208.

(*Z*)-4-(*p*-Tolyl)-1,1,1-trifluorobut-2-en-2-yl trifluoromethanesulfonate (2n). Colorless oil; yield 72% (1.25 g); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, J = 7.7 Hz, 2H), 7.16 (d, J = 7.7 Hz, 2H), 6.54 (t, J = 7.6 Hz, 1H), 3.71 (d, J = 7.6 Hz, 2H), 2.40 (s, 3H). $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ 137.2, 133.8 (q, J = 39.3 Hz), 132.6, 130.3 (dd, J = 5.9 Hz, 2.8 Hz), 129.8, 128.4, 118.7 (q, J = 230.0 Hz), 118.1 (q, J = 241.4 Hz), 31.8, 20.9. ^{19}F NMR (470 MHz, $CDCl_3$) δ -70.01 (m, 3F); -73.10 ~ -73.04 (m, 3F). HRMS (EI) *m/z*: calcd for $C_{12}H_{10}F_6O_3S$ [$M^{+\cdot}$] 348.0255, found: 348.0257.

(*Z*)-4-(3-Chlorophenyl)-1,1,1-trifluorobut-2-en-2-yl trifluoromethanesulfonate (2o). Colorless oil; yield 74% (1.36 g); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 - 7.28 (m, 2H),

7.22 (s, 1H), 7.13 - 7.10 (m, 1H), 6.48 (t, J = 7.5 Hz, 1H), 3.68 (dd, J = 7.5, 1.6 Hz, 2H). $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ 137.6, 134.9, 134.4 (q, J = 31.3 Hz), 130.3, 129.0 (q, J = 3.2 Hz), 128.6, 127.7, 126.6, 118.6 (q, J = 233.4 Hz), 118.4 (q, J = 238.1 Hz), 31.7. ^{19}F NMR (470 MHz, $CDCl_3$) δ -70.15 (m, 3F); -73.06 ~ -73.00 (m, 3F). HRMS (EI) *m/z*: calcd for $C_{11}H_7O_3F_6ClS$ [$M^{+\cdot}$] 367.9709, found: 367.9703.

(*Z*)-4-(Furan-2-yl)-1,1,1-trifluorobut-2-en-2-yl trifluoromethanesulfonate (2p). Colorless oil; yield 67% (1.08 g); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 1.6 Hz, 1H), 6.56 (t, J = 7.4 Hz, 1H), 6.34 (dd, J = 2.9, 2.1 Hz, 1H), 6.18 (d, J = 3.2 Hz, 1H), 3.73 (d, J = 7.4 Hz, 2H). $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ 148.6, 142.3, 134.6 (q, J = 39.5 Hz), 126.9 (q, J = 2.6 Hz), 118.6 (q, J = 233.5 Hz), 118.4 (q, J = 237.8 Hz), 110.5, 107.2, 25.0. ^{19}F NMR (470 MHz, $CDCl_3$) δ -70.41 (m, 3F); -73.27 ~ -73.24 (m, 3F). HRMS (EI) *m/z*: calcd for $C_9H_6F_6O_4S$ [$M^{+\cdot}$] 323.9891, found: 323.9886.

(*Z*)-1,1,1-Trifluorotridec-2-en-2-yl trifluoromethanesulfonate (2q). Colorless oil; yield 74% (563 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.25 (t, J = 7.7 Hz, 1H), 2.26 (m, 2H), 1.42 (m, 2H), 1.25 (m, 14H), 0.80 (t, J = 6.9 Hz, 3H). $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ 133.9 (q, J = 39.1 Hz), 131.2 (q, J = 2.9 Hz), 118.7 (q, J = 228.0 Hz), 118.4 (q, J = 243.0 Hz), 31.8, 29.5, 29.4, 29.2, 29.1, 29.0, 27.7, 26.0, 22.6, 13.8. ^{19}F NMR (470 MHz, $CDCl_3$) δ -70.27 ~ -70.26 (m, 3F); -73.51 ~ -73.44 (m, 3F). HRMS (EI) *m/z*: calcd for $C_{14}H_{22}F_6O_3S$ [$M^{+\cdot}$] 384.1194, found: 384.1189.

General procedure for the preparation of trifluoromethylated diarylethylenes (3).

Under Ar atmosphere, a mixture of **2** (0.5 mmol), tributyl tin compound (0.75 mmol),

$Pd(PPh_3)_2Cl_2$ (10% mmol), LiCl (20% mmol) in dry Toluene (3 mL) was heated to 100 °C for 6-12 h. After reaction completed (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, aqueous KF solution, 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 target material.

(*E*)-1,2-Diphenyl-3,3,3-trifluoroprop-1-ene (3a). Colorless oil; yield 89% (110 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 - 7.37 (m, 3H), 7.30 - 7.28 (m, 2H), 7.24 - 7.12 (m, 4H), 7.00 (d, J = 7.2 Hz, 2H). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 133.6, 133.2 (q, J = 5.9 Hz), 132.8, 130.3 (q, J = 29.3 Hz), 130.1, 129.9, 129.0, 128.9, 128.8, 128.3, 123.8 (q, J = 271.6 Hz). ^{19}F NMR (377 MHz, $CDCl_3$) δ -66.30. HRMS (EI) *m/z*: calcd for $C_{15}H_{11}F_3$ [$M^{+\cdot}$] 248.0813, found: 248.0820. The spectroscopic data correspond to previously reported date.[17b]

(*E*)-1-Phenyl-2-(4-methylphenyl)-3,3,3-trifluoroprop-1-ene (3b).[17c] Colorless oil; yield 84% (110 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 - 7.20 (m, 8H), 7.08 (d, J = 7.2 Hz, 2H), 2.42 (s, 3H). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 138.7, 133.8, 133.0 (q, J = 5.9 Hz), 130.4 (q, J = 29.3 Hz), 130.1, 129.7, 128.8, 128.3, 124.0 (q, J = 273.2 Hz), 21.4. ^{19}F NMR (377 MHz, $CDCl_3$) δ -66.32. HRMS (EI) *m/z*: calcd for $C_{16}H_{13}F_3$ [$M^{+\cdot}$] 262.0969, found: 262.0979.

(*E*)-1-Phenyl-2-(3-methoxylphenyl)-3,3,3-trifluoroprop-1-ene (3c). Colorless oil; yield 87% (120 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (t, J = 7.9 Hz, 1H), 7.20 - 7.13 (m,

4H), 7.03 (d, J = 7.5 Hz, 2H), 6.93 - 6.84 (m, 3H), 3.73 (s, 3H). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 160.0, 134.0, 133.6, 133.3 (q, J = 5.9 Hz), 130.1 (q, J = 29.4 Hz), 129.0, 128.4, 123.9 (q, J = 273.3 Hz), 122.3, 115.3, 114.6, 55.2. ^{19}F NMR (377 MHz, $CDCl_3$) δ -66.17. HRMS (EI) *m/z*: calcd for $C_{16}H_{13}F_3O$ [$M^{+\cdot}$] 278.0918, found: 278.0923.

(*E*)-1-Phenyl-2-(4-methoxylphenyl)-3,3,3-trifluoroprop-1-ene (3d).[17c] Colorless oil; yield 87% (120 mg); ^1H NMR (400 MHz, $CDCl_3$) δ 7.21 - 7.13 (m, 6H), 7.03 (d, J = 7.5 Hz, 2H), 6.90 (d, J = 8.6 Hz, 2H), 3.80 (s, 3H). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 160.0, 133.8, 133.0 (q, J = 5.8 Hz), 131.2, 130.1, 130.0 (q, J = 29.3 Hz), 128.9, 128.3, 124.8, 124.0 (q, J = 273.2 Hz), 114.5, 55.2. ^{19}F NMR (377 MHz, $CDCl_3$) δ -66.39. HRMS (EI) *m/z*: calcd for $C_{16}H_{13}F_3O$ [$M^{+\cdot}$] 278.0918, found: 278.0923.

(*E*)-1-Phenyl-2-(4-chlorophenyl)-3,3,3-trifluoroprop-1-ene (3e).[17c] White solid; yield 85% (120 mg); mp 63.1°C - 63.2 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, J = 8.4 Hz, 2H), 7.24 - 7.16 (m, 6H), 7.01 (d, J = 7.8 Hz, 2H). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 135.0, 133.8 (q, J = 5.8 Hz), 133.2, 131.4, 131.1, 130.0, 129.2 (q, J = 20.0 Hz), 129.1, 129.0, 128.4, 123.6 (q, J = 271.6 Hz). ^{19}F NMR (470 MHz, $CDCl_3$) δ -65.79. HRMS (EI) *m/z*: calcd for $C_{15}H_{10}F_3Cl$ [$M^{+\cdot}$] 282.0423, found: 282.0426.

(*E*)-1-Phenyl-2-(4-formylphenyl)-3,3,3-trifluoroprop-1-ene (3f). White solid; yield 72% (100 mg); mp 46.9 °C - 47.1°C. ^1H NMR (400 MHz, $CDCl_3$) δ 10.04 (s, 1H), 7.90 (d, J = 8.2 Hz, 2H), 7.48 (d, J = 8.2 Hz, 2H), 7.32 (s, 1H), 7.25 - 7.15 (m, 3H), 7.00 (d, J = 7.4 Hz, 2H). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 191.7, 139.1, 134.4 (q, J = 5.8 Hz), 132.9, 130.8, 130.2, 130.0, 129.4, 129.0, 128.5, 123.5 (q, J = 273.4 Hz). ^{19}F NMR (470

MHz, $CDCl_3$) δ -65.24. HRMS (EI) *m/z*: calcd for $C_{16}H_{11}F_3O$ [$M^{+\cdot}$] 276.0762, found: 276.0772.

(*E*)-1-Phenyl-2-allyl-3,3,3-trifluoroprop-1-ene (3g). Colorless oil; yield 100% (106 mg). ^1H NMR (400 MHz, $CDCl_3$) δ 7.40 - 7.33 (m, 5H), 7.18 (s, 1H), 5.96 - 5.87 (m, 1H), 5.17 (dd, *J* = 4.2, 1.5 Hz, 1H), 5.14 (dd, *J* = 3.1, 1.5 Hz, 1H), 3.16 (d, *J* = 5.8 Hz, 2H). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 134.2, 134.1, 133.7 (q, *J* = 6.2 Hz), 129.0, 128.6, 128.5, 128.1, 124.4 (q, *J* = 241.2 Hz), 116.9, 30.7. ^{19}F NMR (377 MHz, $CDCl_3$) δ -67.02. HRMS (EI) *m/z*: calcd for $C_{12}H_{11}F_3$ [$M^{+\cdot}$] 212.0813, found: 212.0822.

(*E*)-1-(3-Methoxylphenyl)-2-(4-methoxyphenyl)-3,3,3-trifluoroprop-1-ene (3h). Colorless oil; yield 98% (150 mg). ^1H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.6 Hz, 2H), 7.16 (d, *J* = 1.4 Hz, 1H), 7.10 (m, 1H), 6.92 (d, *J* = 8.6 Hz, 2H), 6.76 (dd, *J* = 8.2, 2.5 Hz, 1H), 6.67 (d, *J* = 7.6 Hz, 1H), 6.54 (s, 1H), 3.82 (s, 3H), 3.54 (s, 3H). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 159.0, 158.2, 134.0, 131.9 (q, *J* = 5.7 Hz), 130.1, 129.1 (q, *J* = 29.3 Hz), 128.2, 123.8, 122.9 (q, *J* = 273.2 Hz), 121.9, 114.3, 113.4, 54.2, 53.8. ^{19}F NMR (377 MHz, $CDCl_3$) δ -66.55. HRMS (EI) *m/z*: calcd for $C_{17}H_{15}F_3O_2$ [$M^{+\cdot}$] 308.1024, found: 308.1018.

(*E*)-1-(4-Chlorophenyl)-2-(4-methoxylphenyl)-3,3,3-trifluoroprop-1-ene (3i).[29] Colorless oil; yield 90% (140 mg). ^1H NMR (400 MHz, $CDCl_3$) δ 7.17 (d, *J* = 8.4 Hz, 2H), 7.14 - 7.12 (m, 3H), 6.95 (d, *J* = 8.4 Hz, 2H), 6.90 (d, *J* = 8.7 Hz, 2H), 3.81 (s, 3H). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 160.1, 134.7, 132.3, 131.7 (q, *J* = 5.9 Hz), 131.3, 131.0, 130.7 (q, *J* = 29.5 Hz), 128.6, 124.3, 123.8 (q, *J* = 273.3 Hz), 114.6, 55.2. ^{19}F

NMR (377 MHz, $CDCl_3$) δ -66.56. HRMS (EI) *m/z*: calcd for $C_{16}H_{12}ClF_3O$ [$M^{+\cdot}$] 312.0529, found: 312.0536.

(*E*)-1-(3-Chlorophenyl)-2-(4-methoxylphenyl)-3,3,3-trifluoroprop-1-ene (3j). Colorless oil; yield 71% (110 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 - 7.15 (m, 3H), 7.11 (s, 1H), 7.08 - 7.04 (m, 2H), 6.91 - 6.86 (m, 3H), 3.80 (s, 3H). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 160.2, 135.6, 134.2, 131.6 (q, J = 5.9 Hz), 131.5 (q, J = 9.8 Hz), 131.0, 130.0, 129.5, 128.8, 127.9, 124.1, 123.7 (q, J = 273.5 Hz), 114.6, 55.2. ^{19}F NMR (470 MHz, $CDCl_3$) δ -66.19. HRMS (EI) *m/z*: calcd for $C_{16}H_{12}ClF_3O$ [$M^{+\cdot}$] 312.0529, found: 312.0538.

(*E*)-1-(4-Methylphenyl)-2-(4-methoxyphenyl)-3,3,3-trifluoroprop-1-ene (3k). Colorless oil; yield 89% (130 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (d, J = 8.6 Hz, 2H), 7.15 (s, 1H), 6.98 (d, J = 8.6 Hz, 2H), 6.93 - 6.90 (m, 4H), 3.84 (s, 3H), 2.27 (s, 3H). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 158.9, 137.9, 131.9 (q, J = 5.6 Hz), 130.1, 129.9, 129.0, 128.0 (q, J = 33.6 Hz), 124.0, 123.0 (qd, J = 273.2, 1.5 Hz), 113.4, 54.1, 20.1. ^{19}F NMR (470 MHz, $CDCl_3$) δ -65.91. HRMS (EI) *m/z*: calcd for $C_{17}H_{15}F_3O$ [$M^{+\cdot}$] 292.1075, found: 292.1076.

(*E*)-1-(4-Phenyl)phenyl-2-(4-methoxylphenyl)-3,3,3-trifluoroprop-1-ene (3l). Pale yellow soild; yield 100% (190 mg); mp 95.7 °C - 96.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J = 7.4 Hz, 2H), 7.43 - 7.39 (m, 4H), 7.35 - 7.31 (m, 1H), 7.26 - 7.22 (m, 3H), 7.11 (d, J = 8.3 Hz, 2H), 6.94 (d, J = 8.3 Hz, 2H), 3.84 (s, 1H). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 158.9, 140.4, 139.1, 131.7, 131.5 (q, J = 5.8 Hz), 130.1, 129.5, 128.8 (q, J =

29.3 Hz), 127.8, 126.6, 125.9, 125.8, 123.8, 122.9 (q, J = 273.2 Hz), 113.5, 54.2.^{19}F NMR (470 MHz, $CDCl_3$) δ -65.95. HRMS (EI) *m/z*: calcd for $C_{22}H_{17}F_3O$ [$M^{+\cdot}$] 354.1232, found: 354.1242.

(*E*)-1-Naphthyl-2-(4-methoxylphenyl)-3,3,3-trifluoroprop-1-ene (3m). Yellow soild; yield 92% (150 mg); mp 72.1 °C - 72.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 8.3 Hz, 1H), 7.84 (d, J = 9.3 Hz, 2H), 7.71 (d, J = 8.2 Hz, 1H), 7.59 - 7.50 (m, 2H), 7.22 - 7.18 (m, 1H), 7.12 (d, J = 8.7 Hz, 2H), 7.03 (d, J = 7.2 Hz, 1H), 6.73 (d, J = 8.7 Hz, 2H), 3.74 (s, 3H). ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 159.6, 133.4, 132.6 (q, J = 29.0 Hz), 131.9, 131.4 (q, J = 6.0 Hz), 131.3, 131.1, 128.7, 128.6, 127.9, 126.6, 126.2, 125.2, 124.5, 124.0 (q, J = 273.7 Hz), 113.9, 55.1. ^{19}F NMR (470 MHz, $CDCl_3$) δ -65.03. HRMS (EI) *m/z*: calcd for $C_{20}H_{15}F_3O$ [$M^{+\cdot}$] 328.1075, found: 328.1074.

(*E*)-4-Phenyl-2-(4-methoxylphenyl)-1,1,1-trifluorobut-2-ene (3n). Colorless oil; yield 68% (596 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 - 7.28 (m, 2H), 7.24 - 7.20 (m, 3H), 7.11 (d, J = 7.2 Hz, 2H), 6.95 (d, J = 8.7 Hz, 2H), 6.57 (td, J = 7.6, 1.6 Hz,1H), 3.83 (s, 3H), 3.35 (dd, J = 7.6, 1.9 Hz, 2H). ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 159.8, 138.6, 134.6 (q, J = 5.5 Hz), 131.5 (q, J = 29.5 Hz), 131.0, 128.8, 128.4, 126.6, 124.1, 123.6 (q, J = 273.0 Hz), 114.0, 55.3, 34.5. ^{19}F NMR (377 MHz, $CDCl_3$) δ -66.38. HRMS (EI) *m/z*: calcd for $C_{17}H_{15}F_3O$ [$M^{+\cdot}$] 292.1075, found: 292.1083.

(*E*)-2-(4-Methoxylphenyl)-1,1,1-trifluorotridec-2-ene (3o). Colorless oil; yield 65% (110 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (d, J = 8.5 Hz, 2H), 6.92 (d, J = 8.5 Hz, 2H), 6.39 (t, J = 7.5 Hz, 1H), 3.82 (s, 3H), 2.03 - 1.98 (m, 2H), 1.40 - 1.23 (m, 16H), 0.89

(t, J = 6.7 Hz, 3H). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 159.5, 136.7 (q, J = 5.4 Hz), 130.9, 130.6 (q, J = 29.2 Hz), 124.7, 113.8, 55.2, 31.9, 29.6, 29.5, 29.3, 29.1, 28.8, 28.3, 22.7, 14.1. ^{19}F NMR (377 MHz, $CDCl_3$) δ -66.26. HRMS (EI) *m/z*: calcd for $C_{20}H_{29}F_3O$ [$M^{+\cdot}$] 342.2171, found: 342.2169.

(*E*)-1-(4-Chlorophenyl)-2-(3-methoxylphenyl)-3,3,3-trifluoroprop-1-ene (3p). Colorless oil; yield 84% (130 mg). ^1H NMR (400 MHz, $CDCl_3$) δ 7.33 - 7.29 (m, 1H), 7.15 - 7.13 (m, 3H), 6.97 - 6.93 (m, 3H), 6.85 - 6.81 (m, 2H), 3.77 (s, 3H). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 159.0, 133.8, 132.5, 130.9, 130.8 (q, J = 5.9 Hz), 130.2, 129.7 (q, J = 29.5 Hz), 129.2, 127.5, 122.6 (q, J = 273.3 Hz), 121.0, 114.2, 113.5, 54.1.^{19}F NMR (470 MHz, $CDCl_3$) δ -66.43. HRMS (EI) *m/z*: calcd for $C_{16}H_{12}F_3OCl$ [$M^{+\cdot}$] 312.0529, found: 312.0533.

(*E*)-1-(4-Chlorophenyl)-2-(4-methylphenyl)-3,3,3-trifluoroprop-1-ene (3q). White solid; yield 95% (800 mg); mp 56.2 °C - 56.4 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.20 (d, J = 8.0 Hz, 2H), 7.16 - 7.13 (m, 5H), 6.95 (d, J = 8.0 Hz, 2H), 2.39 (s, 3H). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 139.0, 134.8, 132.3, 131.7 (q, J = 5.9 Hz), 131.3, 131.1 (q, J = 29.5 Hz), 129.9, 129.6, 129.3, 128.6, 123.8 (q, J = 273.3 Hz), 21.3. ^{19}F NMR (470 MHz, $CDCl_3$) δ -65.98. HRMS (EI) *m/z*: calcd for $C_{16}H_{12}F_3Cl$ [$M^{+\cdot}$] 296.0580, found: 296.0582.

(*E*)-1-(4-Methylphenyl)-2-(3-methoxylphenyl)-3,3,3-trifluoroprop-1-ene (3r). Colorless oil; yield 76% (110 mg). ^1H NMR (400 MHz, $CDCl_3$) δ 7.32-7.28 (m, 1H), 7.17 (d, J = 1.5 Hz, 1H), 6.98 - 6.92 (m, 5H), 6.88 - 6.84 (m, 2H), 3.77 (s, 3H), 2.27 (s, 3H). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 160.0, 139.2, 134.3, 133.1 (q, J = 5.9 Hz), 130.7,

130.1, 129.1 (d, J = 22.3 Hz), 123.9 (q, J = 273.1 Hz), 115.3, 114.4, 55.2, 21.2.^{19}F NMR (470 MHz, $CDCl_3$) δ -66.13. HRMS (EI) *m/z*: calcd for $C_{17}H_{15}OF_3$ [$M^{+\cdot}$] 292.1075, found: 292.1078.

(*E*)-1-(4-Methylphenyl)-2-phenyl-3,3,3-trifluoroprop-1-ene (3s). Colorless oil; yield 78% (102 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 - 7.39 (m, 3H), 7.31 - 7.28 (m, 2H), 7.18 (s, 1H), 6.96 (d, J = 8.1 Hz, 2H), 6.89 (d, J = 8.1 Hz, 2H), 2.26 (s, 3H). ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 139.2, 133.1 (q, J = 5.9 Hz), 133.0, 130.7, 130.1, 130.0, 129.3 (q, J = 29.2 Hz), 129.1, 129.0, 128.7, 124.0 (q, J = 273.1 Hz), 21.3.^{19}F NMR (470 MHz, $CDCl_3$) δ -65.63. HRMS (EI) *m/z*: calcd for $C_{16}H_{13}F_3$ [$M^{+\cdot}$] 262.0969, found: 262.0973. The spectroscopic data correspond to previously reported date.[30]

General procedure for the preparation of trifluoromethylated enynes (4).

Under Ar atmosphere, a solution of **2** (1.25 mmol or 2.5 mmol), alkyne (1.1 eq), $Pd(PPh_3)_2Cl_2$ (10% mmol), CuI (20% mmol), Et_3N (3.0 eq) in dry THF (5 mL) at room temperature for 12 h. After reaction completed (monitored by TLC), 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 target material.

(*E*)-1-(4-Bromophenyl)-4-phenyl-2-trifluoromethylbut-1-en-3-yne (4a). Yellow soild; Yield 77% (336 mg); mp 72.3 °C - 72.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 8.5 Hz, 2H), 7.57 (d, J = 8.5 Hz, 2H), 7.53 - 7.50 (m, 2H), 7.40 - 7.36 (m, 3H), 7.20 (s,

1H). $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ 136.9 (q, J = 4.7 Hz), 132.4, 131.9, 131.7, 131.1, 129.5, 128.6, 124.7, 122.4 (q, J = 273.5 Hz), 121.0, 112.7 (q, J = 33.7 Hz), 99.5, 81.9. ^{19}F NMR (470 MHz, $CDCl_3$) δ -65.75. HRMS (EI) *m/z*: calcd for $C_{17}H_{10}F_3Br$ [$M^{+\cdot}$] 349.9918, found: 349.9916.

(*E*)-1-(4-Bromophenyl)-4-(4-methylphenyl)-2-trifluoromethylbut-1-en-3-yne (4b). Yellow soild; yield 91% (830 mg); mp 70.6 °C - 71.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 8.5 Hz, 2H), 7.56 (d, J = 8.5 Hz, 2H), 7.41 (d, J = 8.1 Hz, 2H), 7.19 (d, J = 8.1 Hz, 2H), 7.18 (s, 1H), 2.39 (s, 3H). $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ 139.9, 136.4 (q, J = 4.8 Hz), 132.5, 131.8, 131.7, 131.1, 129.4, 124.6, 122.4 (q, J = 273.7 Hz), 118.9, 112.8 (q, J = 33.7 Hz), 99.9, 81.5 (q, J = 1.4 Hz), 21.6. ^{19}F NMR (470 MHz, $CDCl_3$) δ -65.76. HRMS (EI) *m/z*: calcd for $C_{18}H_{12}BrF_3$ [$M^{+\cdot}$] 364.0074, found: 364.0068.

(*E*)-1-(4-Bromophenyl)-4-(3-methylphenyl)-2-trifluoromethylbut-1-en-3-yne (4c). Yellow soild; yield 81% (372 mg); mp 60.1 °C - 60.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 8.6 Hz, 2H), 7.57 (d, J = 8.6 Hz, 2H), 7.34 - 7.28 (m, 3H), 7.23 - 7.20 (m, 2H), 2.37 (s, 3H). $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ 138.4, 136.6 (q, J = 4.7 Hz), 132.5, 132.2, 131.9, 131.1, 130.4, 128.9, 128.5, 124.7, 122.4 (q, J = 273.7 Hz), 121.7, 112.7 (q, J = 33.8 Hz), 99.8, 81.6, 21.2. ^{19}F NMR (470 MHz, $CDCl_3$) δ -65.77. HRMS (EI) *m/z*: calcd for $C_{18}H_{12}BrF_3$ [$M^{+\cdot}$] 364.0074, found: 364.0063.

(*E*)-1-(4-Bromophenyl)-4-(4-chlorophenyl)-2-trifluoromethylbut-1-en-3-yne (4d). Yellow soild; yield 80% (385 mg); mp 88.9 °C - 89.3 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, J = 8.5 Hz, 2H), 7.58 (d, J = 8.5 Hz, 2H), 7.45 (d, J = 8.5 Hz, 2H), 7.37 (d, J =

8.5 Hz, 2H), 7.23 (s, 1H). $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ 137.3 (q, J = 4.8 Hz), 135.7, 132.9, 132.3, 131.9, 131.1, 129.0, 124.9, 122.3 (q, J = 273.7 Hz), 120.3, 112.4 (q, J = 34.0 Hz), 98.1, 82.8 (q, J = 1.4 Hz). ^{19}F NMR (470 MHz, $CDCl_3$) δ -65.70. HRMS (EI) *m/z*: calcd for $C_{17}H_9BrClF_3$ [$M^{+\cdot}$] 383.9528, found: 383.9529.

(*E*)-1-(4-Bromophenyl)-4-(4-methoxylphenyl)-2-trifluoromethylbut-1-en-3-yne (4e). Yellow soild; yield 91% (403 mg); mp 72.3 °C - 72.7 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 8.5 Hz, 2H), 7.56 (d, J = 8.5 Hz, 2H), 7.46 (d, J = 8.9 Hz, 2H), 7.16 (s, 1H), 6.91 (d, J = 8.9 Hz, 2H), 3.85 (s, 3H). $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ 160.7, 135.9 (q, J = 4.8 Hz), 133.3, 132.6, 131.8, 131.1, 124.5, 122.5 (q, J = 273.7 Hz), 114.3, 113.9, 112.8 (q, J = 33.6 Hz), 100.0, 81.1 (q, J = 1.4 Hz), 55.3. ^{19}F NMR (470 MHz, $CDCl_3$) δ -65.78. HRMS (EI) *m/z*: calcd for $C_{18}H_{12}BrF_3O$ [$M^{+\cdot}$] 380.0024, found: 380.0032.

(*E*)-1-(4-Bromophenyl)-4-(3-aminophenyl)-2-trifluoromethylbut-1-en-3-yne (4f). Yellow soild; yield 81% (372 mg); mp 96.7 °C - 97.0 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, J = 8.5 Hz, 2H), 7.54 (d, J = 8.5 Hz, 2H), 7.17 - 7.13 (m, 2H), 6.91 (d, J = 7.5 Hz, 1H), 6.80 (s, 1H), 6.70 (d, J = 7.5 Hz, 1H), 3.72 (s, 2H). $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ 146.5, 136.7 (q, J = 4.7 Hz), 132.4, 131.9, 131.2, 129.6, 124.7, 122.5, 122.4 (q, J = 273.8 Hz), 122.1, 117.6, 116.5, 112.6 (q, J = 33.8 Hz), 99.9, 81.3 (q, J = 1.2 Hz).^{19}F NMR (470 MHz, $CDCl_3$) δ -65.76. HRMS (EI) *m/z*: calcd for $C_{17}H_{11}BrF_3N$ [$M^{+\cdot}$] 365.0027, found: 365.0030.

(*E*)-1-(4-Bromophenyl)-2-trifluoromethyloct-1-en-3-yne (4g). Colorless oil; yield 90% (745 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 8.6 Hz, 2H), 7.49 (d, J = 8.6 Hz,

2H), 7.05 (s, 1H), 2.46 (t, J = 7.0 Hz, 2H), 1.64 - 1.57 (m, 2H), 1.51 - 1.44 (m, 2H), 0.95 (t, J = 7.3 Hz, 3H). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 135.6 (q, J = 4.9 Hz), 132.5, 131.7, 130.9, 124.2, 122.5 (q, J = 273.5 Hz), 113.0 (q, J = 33.4 Hz), 102.1, 73.4 (q, J = 1.5 Hz), 30.2, 22.0, 19.5, 13.5. ^{19}F NMR (470 MHz, $CDCl_3$) δ -66.32. HRMS (EI) *m/z*: calcd for $C_{15}H_{14}BrF_3$ [$M^{+\cdot}$] 330.0231, found: 330.0238.

(*E*)-1,4-Di(4-methylphenyl)-2-trifluoromethylbut-1-en-3-yne (4h). White soild; yield 84% (750 mg); mp 70.6 °C - 70.9 °C.^1H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8.1 Hz, 2H), 7.43 (d, J = 8.1 Hz, 2H), 7.25 - 7.23 (m, 3H), 7.18 (d, J = 8.1 Hz, 2H), 2.40 (s, 3H), 2.38 (s, 3H). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 140.9, 139.5, 137.8 (q, J = 4.7 Hz), 131.6, 130.9, 129.8, 129.34, 129.31, 122.7 (q, J = 273.2 Hz), 119.3, 110.9 (q, J = 33.5 Hz), 98.8, 82.0 (q, J = 1.4 Hz), 21.6, 21.5. ^{19}F NMR (470 MHz, $CDCl_3$) δ -65.47. HRMS (EI) *m/z*: calcd for $C_{19}H_{15}F_3$ [$M^{+\cdot}$] 300.1126, found: 300.1133.

(*E*)-1-(4-Methylphenyl)-4-phenyl-2-trifluoromethylbut-1-en-3-yne (4i). Colorless oil; yield 95% (138 mg). ^1H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 8.1 Hz, 2H), 7.53 - 7.50 (m, 2H), 7.36 - 7.33 (m, 3H), 7.23 (s, 1H), 7.22 (d, J = 8.1 Hz, 2H), 2.37 (s, 3H). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 141.0, 138.3 (q, J = 4.7 Hz), 131.7, 130.9, 129.9, 129.4, 129.2, 128.5, 122.7 (q, J = 273.8 Hz), 122.3, 110.8 (q, J = 33.6 Hz), 98.5, 82.5, 21.6. ^{19}F NMR (470 MHz, $CDCl_3$) δ -65.44. HRMS (EI) *m/z*: calcd for $C_{18}H_{13}F_3$ [$M^{+\cdot}$] 286.0969, found: 286.0975.

(*E*)-1-Phenyl-4-(4-methoxylphenyl)-2-trifluoromethylbut-1-en-3-yne (4j). Colorless oil; yield 100% (151 mg). ^1H NMR (400 MHz, $CDCl_3$) δ 7.99 - 7.96 (m, 2H), 7.48 (d, J =

8.9 Hz, 2H), 7.44 - 7.40 (m, 3H), 7.24 (d, J = 1.3 Hz, 1H), 6.90 (d, J = 8.9 Hz, 2H), 3.84 (s, 3H). $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ 160.5, 137.4 (q, J = 4.7 Hz), 133.7, 133.3, 130.3, 129.8, 128.6, 122.6 (q, J = 273.5 Hz), 114.3, 112.2 (q, J = 33.4 Hz), 99.0, 81.3 (q, J = 1.5 Hz), 55.3. ^{19}F NMR (470 MHz, $CDCl_3$) δ -65.64. HRMS (EI) *m/z*: calcd for $C_{18}H_{13}OF_3$ [$M^{+\cdot}$] 302.0918, found: 302.0919.

General procedure for the preparation of trifluoromethylated alkynes (5).

A solution of **2** (1.3 mmol), Et_3N (1.5 eq) in dry DMF (3 mL) was stirred at 30 °C for 12 h. After reaction completed (monitored by TLC), 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 target material.

1-(2-Bromophenyl)-3,3,3-trifluoroprop-1-yne (5a). Colorless oil; yield 90% (290 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 - 7.62 (m, 1H), 7.60 - 7.56 (m, 1H), 7.38 - 7.31 (m, 2H). The spectroscopic data correspond to previously reported date.[31a]

1-(4-Bromophenyl)-3,3,3-trifluoroprop-1-yne (5b). Colorless oil; yield 99% (320 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 8.5 Hz, 2H), 7.42 (d, J = 8.5 Hz, 2H). The spectroscopic data correspond to previously reported date.[31a]

1-(4-Phenyl)phenyl-3,3,3-trifluoroprop-1-yne (5c). White solid; yield 88% (280 mg); mp 85.7 °C - 85.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 - 7.58 (m, 6H), 7.49 - 7.45 (m, 2H), 7.42 - 7.37 (m, 1H). The spectroscopic data correspond to previously reported

date.[31b]

1-Naphthyl-3,3,3-trifluoroprop-1-yne (5d). Colorless oil; yield 98% (110 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, J = 8.3 Hz, 1H), 7.98 (d, J = 8.3 Hz, 1H), 7.90 (d, J = 8.2 Hz, 1H), 7.82 (d, J = 7.1 Hz, 1H), 7.67 - 7.56 (m, 2H), 7.50 - 7.46 (m, 1H). The spectroscopic data correspond to previously reported date.[31c]

1-(4-Tolylthio)-3,3,3-trifluoroprop-1-yne (5e). Colorless oil; yield 67% (145 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, J = 8.3 Hz, 2H), 7.20 (d, J = 8.3 Hz, 2H), 2.36 (s, 3H). ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 138.8, 130.6, 128.7, 124.6 (d, J = 0.9 Hz), 114.4 (q, J = 257.4 Hz), 82.9 (q, J = 53.3 Hz), 80.2 (q, J = 6.9 Hz), 20.9. ^{19}F NMR (470 MHz, $CDCl_3$) δ -49.56. HRMS (EI) *m/z*: calcd for $C_{10}H_7SF_3$ [$M^{+\cdot}$] 216.0221, found: 216.0225.

General procedure for the preparation of 3-trifluoromethylbenzofurans (6).

Under Ar atmosphere, a mixture of **2** (0.5 mmol), $KHCO_3$ (2.0 eq) in dry DMF (5 mL) was stirred at 30 °C for 12 h. After reaction completed (monitored by TLC), $Pd_2(dba)_3$ (10% mmol), P(*t*-Bu)$_3$ (10wt% in toluene, 0.8 eq), K_2CO_3 (5.0 eq) and 2-iodophenol (1.2 eq) were added. After being heated for 12 h at 140 °C, the mixture was quenched with 10% $NaHCO_3$ 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 target material.

2-(Tolyl)-3-(trifluoromethyl)benzofuran (6a). White solid; yield 60% (83 mg); mp 69.3 °C - 69.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 7.7 Hz, 1H), 7.72 (d, J =

8.1 Hz, 2H), 7.55 (d, *J* = 7.7 Hz, 1H), 7.40 - 7.34 (m, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 2.44 (s, 3H). The spectroscopic data correspond to previously reported date.[20b]

2-(3-Chlorophenyl)-3-(trifluoromethyl)benzofuran (6b). Colorless oil; yield 61% (91 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.77 (d, *J* = 7.2 Hz, 1H), 7.71 (d, *J* = 7.2 Hz, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.49 - 7.35 (m, 4H). The spectroscopic data correspond to previously reported date.[20b]

2-(3-Methoxyphenyl)-3-(trifluoromethyl)benzofuran (6c). Colorless oil; yield 50% (73 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.5 Hz, 1H), 7.57 (d, *J* = 7.9 Hz, 1H), 7.44 - 7.34 (m, 5H), 7.07 - 7.04 (m, 1H), 3.90 (s, 3H). The spectroscopic data correspond to previously reported date.[20b]

2-(Biphenyl-4-yl)-3-(trifluoromethyl)benzofuran (6d). White solid; yield 61% (103 mg); mp 79.6 °C - 80.1 °C . ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.3 Hz, 2H), 7.78 (d, *J* = 7.7 Hz, 1H), 7.74 (d, *J* = 8.3 Hz, 2H), 7.67 (d, *J* = 7.4 Hz, 2H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.49 (m, 2H), 7.39 (m, 3H). The spectroscopic data correspond to previously reported date.[20b]

Procedure for the preparation of 7

(*Z*)-4-(3-Methyl-4-ethoxycarbonyl)phenyl-1,1,1-trifluorobut-2-en-2-yl trifluoromethanesulfonate (2r). In a similar method, **2r** was obtained from **1r** (0.37 g, 1.34 mmol). Colorless oil; yield 82% (460 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.6 Hz, 1H), 7.09 - 7.08 (m, 2H), 6.48 (t, *J* = 7.6 Hz, 1H), 4.36 (q, *J* = 7.1 Hz, 2H), 3.68 (dd, *J* = 7.6 Hz, 1.3 Hz, 2H), 2.60 (s, 3H), 1.39 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H}NMR (100

MHz, $CDCl_3$) δ 166.2, 140.0, 138.4, 133.3 (q, J = 39.4 Hz), 130.8, 130.4, 128.2 (q, J = 3.4 Hz), 128.1, 124.8, 117.6 (q, J = 286.9 Hz), 117.3 (q, J = 306.1 Hz), 59.8, 30.8, 20.7, 13.3. ^{19}F NMR (470 MHz, $CDCl_3$) δ -69.98 ~ -69.95 (m, 3F), -72.82 (q, J = 4.5 Hz, 3F). HRMS (EI) *m/z*: calcd for $C_{15}H_{14}O_5F_6S$ [$M^{+\cdot}$] 420.0466, found: 420.0463.

(*E*)-4-(3-Methyl-4-ethoxycarbonyl)phenyl-2-(3,5-dichloro)phenyl-1,1,1-trifluorobut-2-ene (3t). 3t was obtained from **2r** (0.42 g, 1 mmol). Colorless oil; yield 100% (417 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 7.9 Hz, 1H), 7.44 (s, 1H), 7.19 (d, J = 0.9 Hz, 2H), 6.98 - 6.95 (m, 2H), 6.63 (td, J = 7.7 Hz, 0.9 Hz, 1H), 4.35 (q, J = 7.1 Hz, 2H), 3.34 (dd, J = 7.7 Hz, 1.1 Hz, 2H), 2.59 (s, 3H), 1.39 (t, J = 7.1 Hz, 4H). ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 166.2, 140.5, 139.9, 134.7 (q, J = 5.4 Hz), 134.4, 133.5, 130.6, 130.2, 129.1 (q, J = 30.5 Hz), 128.2, 127.6, 127.2, 124.6, 121.7 (q, J = 273.0 Hz), 59.7, 33.2, 20.7, 13.3. ^{19}F NMR (470 MHz, $CDCl_3$) δ -65.74. HRMS (EI) *m/z*: calcd for $C_{20}H_{17}O_2F_3Cl_2$ [$M^{+\cdot}$] 416.0558, found: 416.0555.

(*E*)-1-(3-Methyl-4-ethoxycarbonyl)phenyl-3-(3,5-dichloro)phenyl-4,4,4-trifluorobut-1-ene (7).[26] Under Ar atmosphere, a mixture of **3t** (0.1 mmol), $Pd(OAc)_2$ (40% mmol), Xantphos (40% mmol), DMSO (3.2 eq) in dry DMF (1 mL) was stirred at 120 °C for 12 h. After reaction completed (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 target material. Colorless oil; yield 65% (27

mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 8.6 Hz, 1H), 7.15 (m, 5H), 6.46 (d, J = 15.9 Hz, 1H), 6.30 (dd, J = 15.9 Hz, 8.0 Hz, 1H), 4.24 (q, J = 7.1 Hz, 2H), 3.99 (m, 1H), 2.49 (s, 3H), 1.28 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H}NMR (126 MHz, $CDCl_3$) δ 166.2, 139.6, 137.7, 136.5, 134.7, 134.5, 130.1, 128.9, 128.7, 127.7, 126.5, 124.3 (q, J = 280.5 Hz), 122.8, 122.1 (d, J = 2.3 Hz), 59.8, 51.9 (q, J = 28.5 Hz), 20.8, 13.3. ^{19}F NMR (470 MHz, $CDCl_3$) δ -68.61 (d, J = 9.4 Hz). HRMS (EI) *m/z*: calcd for $C_{20}H_{17}O_2F_3Cl_2$ [$M^{+\cdot}$] 416.0558, found: 416.0564.

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Notes

The authors declare no competing financial interest.

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ASSOCIATED CONTENT

Supporting Information

NMR spectra for all compounds. The crystal structure determination of **2e** and **3q**. This material is available free of charge via the Internet at http://pubs.acs.org.

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