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Graphical Abstract

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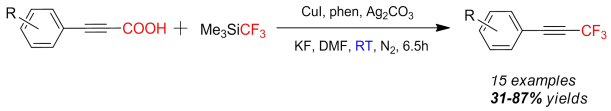

15 examples
***31-87%** yields*

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Cu(I)/Ag(I)-Mediated Decarboxylative Trifluoromethylation of Arylpropiolic Acids with Me_3SiCF_3 at Room Temperature

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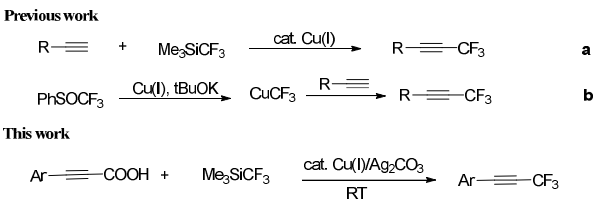
ABSTRACT

A novel Cu(I)/Ag(I)-mediated decarboxylative trifluoromethylation of arylpropiolic acids with Me_3SiCF_3 has been developed for the construction of Csp-CF_3 bond under mild conditions. This method proceeds smoothly at room temperature and shows a widely functional compatibility, providing a series of corresponding trifluoromethylated acetylenyl-containing aromatics in good yields.

1. Introduction

The trifluoromethyl derivatives are widely used in agrochemicals, pharmaceuticals and materials,[1,2] since incorporation of trifluoromethyl groups into the organic molecules brings remarkable changes in their physical, chemical, and biological properties because of the strong electronic properties, lipophilicity and metabolic stability of the trifluoromethyl group.[1] Although a number of methods for the construction of Csp^3-CF_3 bonds[3,4] and Csp^2-CF_3 bonds[4e,5] have been reported during the past years, few reactions are applicable for the construction of Csp-CF_3 bonds.[5g,6,7] In addition, few reactions with nucleophilic reagents have been studied. Recently, the Qing's group (Scheme 1a)[6] and Hu's group(Scheme 1b)[7a] have successfully discovered the possibility of generating "Cu-CF_3"complex from Cu(I) salts and nucleophilic trifluoromethylating reagents respectively. The kind of complex could be reacted with terminal alkynes, affording the corresponding trifluoromethylated arylacetylenes in good yields. Usually, terminal alkynes have been employed as alkyne sources



Scheme 1. Formation of Csp-CF_3bond with nucleophilic trifluoromethylating reagents

for the synthesis of Csp-CF_3 bonds. However, there is a limitation that some of terminal alkynes are cumbersomely handled because of their relatively low boiling points.[8]

Compared to terminal alkynes, the arylpropiolic acids as alkyne sources have many advantages. They are usually solid-state without strong smells and easy to store and handle.[9,10a-c] Besides, the synthetic procedures and purification of arylpropiolic acids are easier and simpler.[10d] Therefore, using arylpropiolic acids as alkyne sources would make the process safer and easier to operate.[10c,12f]Since 2008, a variety of decaroxylative coupling reactions of alkynyl carboxylic acids have been developed by Lee's group[8,10,11] and others,[12,13] including the formation of C-C, C-N, C-S, C-P bonds. However, decarboxylative coupling reactions with Csp^3 groups are rare. Lee's group[10d] and Satya[12g] et al respectively reported that the decarboxylative coupling reaction of arylpropiolic acids with ICH_2CH_3 and S_N2' allylic coupling of acetates of the Baylis–Hillman alcohols form the corresponding $Csp-Csp^3$ bonds directly. As far as we know, the formation of Csp-CF_3 bonds through the coupling of arylpropiolic acids with trifluoromethylating reagents has not been reported. Instead of CF_3-substituted alkynes, Hu's group[14] obtained the α-trifluoromethyl ketones using phenylpropiolic acid as the substrate. Herein, we developed a new and mild process for Cu(I)/Ag(I)-mediated decarboxylative trifluoromethylation of arylpropiolic acids at room temperature to construct Csp-CF_3 bond by using cheap Me_3SiCF_3.

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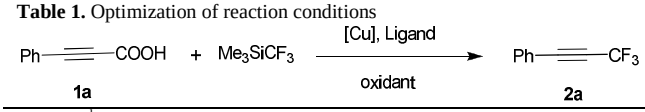
Table 1. Optimization of reaction conditions



1a 2a

Entry[a,b]	Catalyst[Cu]	Ligand	Oxidant	Yield of 2**a** %
1[c]	CuI (1.0 equiv), 70 ℃	phen (1.0 equiv)	Ag_2CO_3 (2.0 equiv)	33
2[c]	CuI (1.0 equiv), r.t.	phen (1.0 equiv)	Ag_2CO_3 (2.0 equiv)	38
3	CuI (1.0 equiv), r.t.	phen (1.0 equiv)	Ag_2CO_3 (2.0 equiv)	89
4	CuBr (1.0 equiv), r.t.	phen (1.0 equiv)	Ag_2CO_3 (2.0 equiv)	77
5	CuCl (1.0 equiv), r.t.	phen (1.0 equiv)	Ag_2CO_3 (2.0 equiv)	72
6	$Cu(OAc)_2$ (1.0 equiv), r.t.	hen (1.0 equiv)	Ag_2CO_3 (2.0 equiv)	n.r
7	CuI (1.0 equiv), r.t.	bpy (1.0 equiv)	Ag_2CO_3 (2.0 equiv)	77
8	CuI (1.0 equiv), r.t.	TMEDA (1.0 equiv)	Ag_2CO_3 (2.0 equiv)	83
9	CuI (1.0 equiv), r.t.	phen (1.0 equiv)	Air	21
10	CuI (1.0 equiv), r.t.	phen (1.0 equiv)	O_2	23
11	CuI (1.0 equiv), r.t.	phen (1.0 equiv)	$Cu(OAc)_2$ (2.0 equiv)	16
12[d]	CuI (1.0 equiv), r.t.	phen (1.0 equiv)	Ag_2CO_3 (2.0 equiv)	20
13	CuI (0.5 equiv), r.t.	phen (0.5equiv)	Ag_2CO_3 (2.0 equiv)	78
14[e]	CuI (0.1 equiv), r.t.	phen (0.1equiv)	Ag_2CO_3 (2.0 equiv)	11
15	CuI(1.0 equiv), r.t.	phen (1.0 equiv)	Ag_2CO_3 (1.0 equiv)	57

[a] Reaction conditions: **1a** (0.1 mmol), Me_3SiCF_3 (5.0 equiv), KF (3.0 equiv), DMF (2.5 ml), N_2, r.t., 6.5 h. Phenylpropiolic acid was introduced slowly *via* syringe pump over four hours. phen=1,10-phenanthroline.

[b] Yields were as determined by GC analysis, using n-dodecane as internal standard.

[c] Phenylpropiolicacid was mixed with other raw materials at one pot.

[d] Me_3SiCF_3 (3.0 equiv).

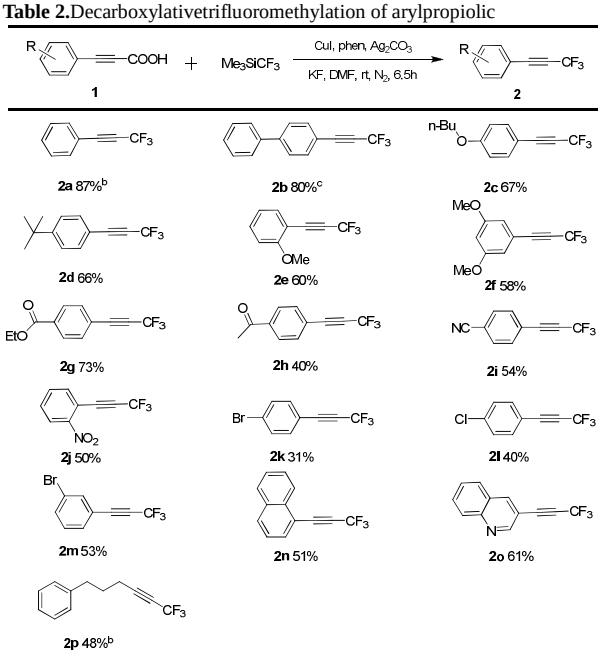
2. Results and discussion

Initially, Cu(I)/Ag(I) mediated decarboxylative trifluoromethylation of phenylpropiolic acid (**1a**) with Me_3SiCF_3 in DMF to give the corresponding trifluoromethylated product **2a** was employed as a model reaction (Table 1). When a mixture of **1a** (0.1 mmol), Me_3SiCF_3 (5.0 equiv), KF (3.0 equiv), Ag_2CO_3 (2.0 equiv), and CuI/phen (1.0 equiv) in DMF was reacting at 70℃ for 24 h under nitrogen atmosphere, **2a** was formed in 33% yield (Table 1, Entry 1), and the homocoupling byproduct diphenylacetylene was obtained in high yield (50%).When the reaction was carried out at room temperature, the yield of **2a** was almost the same as that at 70℃ (Table 1, Entry 2). We speculated that the rate of decarboxylative homocoupling was much faster than that of trifluoromethylation, the high concentration of phenylpropiolic acid lead to high yield of byproduct diphenylacetylene. In order to inhibit the homocoupling byproduct, we used a syringe pump to introduce **1a** in droplet over a period of 4 h to the mixture of Me_3SiCF_3, KF, Ag_2CO_3, and CuI/phen in DMF at room temperature under N_2 atmosphere. To our delight, the yield of **2a** was improved to 89% as determined by GC analysis (Table 1, Entry 3). Subsequently we explored the effects of other reagents on this reaction. CuI as a catalyst showed more efficient than CuBr and CuCl (Table 1, Entries 4 and 5), whereas $Cu(OAc)_2$ gave poor performance (Table 1, Entry 6). Screening other ligands, 2,2'-bipyridine (Bpy), *N,N,N',N'*-tetramethylethylenediamine (TMEDA) showed poor results (Table 1, Entries 7 and 8). Moreover, for the oxidants, Ag_2CO_3 was better than air, O_2 and $Cu(OAc)_2$ (Table 1, Entries 9-11). When the amount of Me_3SiCF_3 was reduced to 3.0 equivalents, only 20% yield of **2a** was obtained (Table 1, Entry 12). Decreasing the amount of CuI/phen or Ag_2CO_3 resulted in lowering yields of **2a** respectively (Table 1, Entries 13-15).

With the optimal reaction conditions in hand, we next investigated the substrate scope of decarboxylative trifluoromethylation of arylpropiolic acids (Table 2). Many functional groups, such as alkoxy, ester, nitro, acetyl, halogen, could be well-tolerated under the optimal conditions. Arylpropiolic acids bearing electron-donating groups (phenyl, butoxy, *tert*-butyl, methoxyl) at either *para*- or *ortho*-positions proceeded with Me_3SiCF_3 smoothly to give the corresponding products in modest to good yields (Table 2, **2b-e**, 60%-80%). Reaction of arylpropiolic acids that bearing two electron-donating groups such as 3,5-dimethoxy also gave 58% yield of **2f**. Arylpropiolic acids bearing electron-withdrawing groups (acetyl, cyan, nitryl) at either *para*- or *ortho*- position, gave relatively low yields of desired products (Table 2, **2h-j**, 40%-54%). Noteworthy is that ester group at *para*-position was well compatible with the screening condition (Table 2, **2g**, 73%). Reactions of the halogen-substituted phenylpropiolic acids, such as 3-bromo, 4-bromo and 4-chloro, could result in a drop in reaction yields (**2m** 53%, **2k** 31% and **2l** 40%) respectively. Naphthylpropiolic acid gave a fair yield (Table 2, **2n**, 51%). Gratifyingly, for the *N*-heterocyclic aromatics, the quinolylpropiolic acid also carried out in a good yield of 61%

(Table 2, **2o**). In addition, alkylpropiolic acid-6-phenylhex-2-ynoic acid could also be compatible with this system and

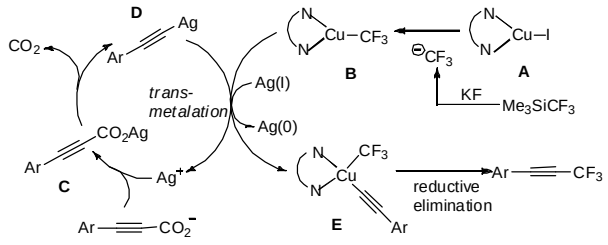
Table 2. Decarboxylativetrifluoromethylation of arylpropiolic



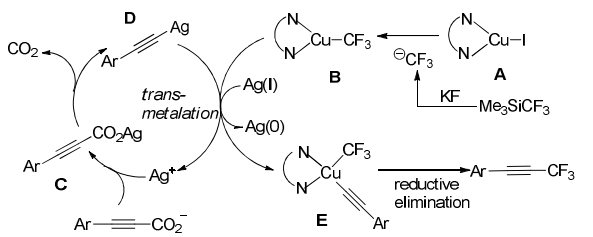
[a] Reaction conditions: arylpropiolic acid (0.4 mmol), Me_3SiCF_3(2.0 mmol), CuI (0.4 mmol), phen (0.4 mmol), Ag_2CO_3(0.8 mmol), KF (1.2 mmol), DMF (6.0 mL), N_2, rt, 6.5 h, isolated yields.
[b] Yield of **2a** was determined by the ^{19}F NMR with phenyl trifluoromethyl sulfide as an internal standard.
[c] Isolated yield of 0.2 mmol **2b**.

obtained the moderate yield (Table 2, **2p**, 48%).

Based on the previous work,[6,12d,g,15,16] a plausible mechanism for the decarboxylative trifluoromethylation of arylpropiolicacids with Me_3SiCF_3 was proposed. As shown in Scheme 2**,** a complex [(phen)CuI] **A** would be generated when the reaction started with CuI and phen in DMF. The generation of trifluoromethyl anion could then follow to form the key $CuCF_3$intermediate **B**. Subsequent the transmetalation between alkynyl metal-silver species **D** and **B** occurred to form **E** in the presence of Ag_2CO_3. The complex **D** might be generated from decarboxylation of silver carboxylates **C**. Finally, the reductive elimination of complex **E** delivered the target compound.



Scheme 2. Plausible mechanism for decarboxylative trifluoromethylation of arylpropiolic acids



Scheme 2. Plausible mechanism for decarboxylative trifluoromethylation of arylpropiolic acids

3. Conclusions

In summary, we have developed a new and effective method for the construction of a Csp-CF_3 bond via a Cu(I)/Ag(I) mediated decarboxylative trifluoromethylation of arylpropiolic acids with Me_3SiCF_3 under relatively mild conditions. This method tolerates a variety of functional groups and provides a direct route to produce various trifluoromethylated alkynes. Since both the salts of carboxylic acids and Me_3SiCF_3 are easily available, this room temperature decarboxylative trifluoromethylation method will have great advantages for academic and industrial research.

4. Experimental Section

4.1. General procedures

All reagents were obtained from commercial sources (>99%) and used without further purification unless otherwise noted. Anhydrous potassium fluoride (KF) was dried in a vacuum-oven at 200 ℃ for 24 h and stored in a N_2 filled glove box. Anhydrous N,N'- dimethylformamide (DMF) was dispensed from a solvent purification system. Analytical thin layer chromatography (TLC) was carried out with silica gel GF_{254} precoated plates. Visualization was accomplished with a UV lamp. The reactions were carried out under nitrogen atmosphere and the products were isolated by column chromatography on silica gel (200-300 mesh) using dichloromethane / petroleum ether (PE, 30-60℃) (v/v, 0-1/2). All compounds were characterized by ^1H NMR, ^{13}C NMR, ^{19}F NMR and Mass spectrometry. ^1H NMR spectra were recorded on Varian INOVA 400M and Bruker 500M instruments. ^{13}C NMR and ^{19}F NMR spectra were recorded on a Bruker 500M instruments. Chemical shifts (δ) are reported in ppm with TMS as internal standard. Gas chromatography analyses were performed with an FID detector. GC-MS data was also performed.

4.1. General procedure for synthesis of arylpropiolic acids

Compounds(1**b**-1**o**)were prepared according to literature.[17] To a mixture of $Pd(PPh_3)_2Cl_2$ (70 mg, 2 mol %), CuI (38 mg, 4 mol %) and DMF (7 mL) taken in a flask, aryl iodide (5.0 mmol), propiolic acid (414 mg, 6.0 mmol) and diisopropylamine (1.30 g, 12.5 mmol) were added in that sequence under nitrogen atmosphere. After stirring the reaction mixture at room temperature for 5 h, the resulting mixture was diluted with ethyl acetate, filtered through celite bed, the filtrate was washed with cold aqueous KOH solution (1 × 100 mL) and acidified with dilute sulfuric acid (10% solution) at 0 ℃. The solid obtained was extracted with dichloromethane and the extract was washed with water, brine solution and dried over anhydrous sodium sulfate. The organic layer was concentrated in vacuum at 40 ℃, dried to get the arylpropiolic acids.

4.2. General procedure for Cu(I)/Ag(I)-mediated decarboxylative trifluoromethylation of arylpropiolic acids with Ruppert–Prakash reagent (0.4 mmol Scale)

A mixture of CuI (76 mg, 0.4 mmol), phen (79 mg, 0.4 mmol), Ag_2CO_3 (220 mg, 0.8 mmol), KF (69 mg, 1.2 mmol) and DMF (6 mL) was added to a 25mL round-bottom flask that was equipped with a magnetic stir bar at room temperature in a glove box. The round-bottom flask was sealed with a rubber plug and taken out. Then the flask was evacuated and refilled with nitrogen for three times. Next, Me_3SiCF_3 (294 μL, 2.0 mmol) was added to the mixture dropwise in five minutes and the mixture was stirred at room temperature for 30 minutes. A solution of arylpropiolic acids (0.4 mmol) in 1.0 mL DMF was added to the flask during 4 h by using a syringe pump at room temperature. After the addition, the reaction mixture was kept for another 2 h at room

temperature. At the end of reaction, dichloromethane (DCM) was added to the reaction system. The organic layer was separated and washed with water three times. The combined organic extracts was dried over Na_2SO_4 for 2h and then concentrated under vacuum. After evaporation, the residue was purified by silica gel column chromatography with petroleum ether to provide pure desired products.

*4.3.1 4-(3,3,3-Trifluoroprop-1-yn-1-yl)-1,10-biphenyl (**2b**):*White solid (39 mg, 80% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 – 7.59 (m, 6H), 7.51 – 7.46 (m, 2H), 7.45 – 7.39 (m, 1H).^{13}C NMR (126 MHz, $CDCl_3$) δ 143.73, 139.70, 132.90 (q, *J* = 1.5 Hz), 129.01, 128.25, 127.30, 127.15, 117.22 (d, *J* = 1.8 Hz), 114.94(q, *J* = 257.0 Hz), 86.56 (q, *J* = 6.4 Hz), 76.23 (q, *J* = 52.7 Hz). ^{19}F NMR (470 MHz, $CDCl_3$) δ -49.67 (s, 3F). GC-MS (EI): m/z = 246 (M^+).

*4.3.2 1-Butoxy-4-(3,3,3-trifluoroprop-1-ynyl)benzene (**2c**):*Colorless oil (65 mg, 67% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.5 Hz, 2H), 6.86 (d, *J* = 8.5 Hz, 2H), 3.97 (t, *J* = 6.4 Hz, 2H), 1.80 – 1.73 (m, 2H), 1.55 – 1.44 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 161.21, 134.12 (q, *J*= 1.3 Hz), 115.12(q, *J* = 257.0 Hz) , 114.79, 110.02 (q, *J* = 1.7 Hz), 87.23 (q, *J* = 6.4 Hz), 73.73 (q, *J* = 51.7 Hz), 67.92, 31.12, 19.17, 13.74. ^{19}F NMR (470 MHz, $CDCl_3$) δ -49.38 (s, 3F).GC-MS (EI): m/z 242 (M^+).

*4.3.3 1-tert-butylphenyl-4-(3,3,3-trifluoroprop-1-ynyl)benzene (**2d**):*Yellow solid (60 mg, 66% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ7.48 (d, *J* = 8.3 Hz, 2H), 7.40 (d, *J* = 8.3 Hz, 2H), 1.32 (s, 9H).^{13}C NMR (126 MHz, $CDCl_3$) δ 154.55 (s), 132.25 (q, *J* = 1.4 Hz), 125.69, 116.00, 115.44 (q, *J* = 1.8 Hz), 113.96, 86.93 (q, *J* = 6.4 Hz), 75.22(q, *J* = 52.5 Hz) , 35.04, 31.01. ^{19}F NMR (470 MHz, $CDCl_3$) δ -49.57 (s, 3F). GC-MS (EI): m/z 226 (M^+).

*4.3.4 1-Methoxy-2-(3,3,3-trifluoroprop-1-ynyl)benzene (**2e**):* Yellow oil (48 mg, 60% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.42 (m, 2H), 7.01 – 6.90 (m, 2H), 3.92 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.30, 133.34 (q, *J* = 1.3 Hz), 131.47, 119.51, 114.03 (q, *J* = 257.0 Hz), 113.32, 82.76 (q, *J* = 6.4 Hz), 78.32 (q, *J* = 51.7 Hz). ^{19}F NMR (470 MHz, $CDCl_3$) δ -49.45 (s, 3F). GC-MS (EI): m/z 220 (M^+).

*4.3.5 1,3-dimethoxy-5-(3,3,3-trifluoroprop-1-ynyl)benzene (**2f**):* Yellow oil (54 mg, 58% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.61 (d, *J* = 2.3 Hz, 2H), 6.48 (t, *J* = 2.3 Hz, 1H), 3.72 (s, 6H).^{13}C NMR (126 MHz, $CDCl_3$) δ 160.70, 119.64 (q, *J* = 1.8 Hz), 114.78(q, *J* = 257.4 Hz), 110.11, 104.19, 86.50 (q, *J* = 6.4 Hz), 75.00 (q, *J* = 52.8 Hz), 55.49. ^{19}F NMR (470 MHz, $CDCl_3$) δ -49.84 (s, 3F). GC-MS (EI): m/z 230 (M^+).

*4.3.6 Ethyl -4-(3,3,3-trifluoroprop-1-yn-1-yl)benzoate (**2g**):* Colorless oil (71 mg, 73% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.3 Hz, 2H), 7.63 (d, *J* = 8.3 Hz, 2H), 4.40 (q, *J* = 7.1 Hz, 2H), 1.41 (t, *J* = 7.1 Hz, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 164.43, 131.50, 131.38(q, *J* = 1.3 Hz), 128.65, 121.71 (q, *J* = 1.8 Hz), 113.64 (q, *J* = 258.3 Hz), 84.34 (q, *J* = 6.5 Hz), 76.68(q, *J* = 53.0 Hz), 60.50, 13.23. ^{19}F NMR (470 MHz, $CDCl_3$) δ -50.22 (s, 3F). GC-MS (EI): m/z 242 (M^+).

*4.3.7 1-Acetyl--4-(3,3,3-trifluoroprop-1-ynyl)benzene (**2h**):* White solid (34 mg, 40% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.4 Hz, 2H), 7.66 (d, *J* = 8.4 Hz, 2H), 2.63 (s, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 196.91, 138.38, 132.69 (q, *J* = 1.0 Hz), 128.35, 122.92 (d, *J* = 1.6 Hz), 114.60(q, *J* = 258.3 Hz), 85.17 (q, *J* = 6.4 Hz), 77.93(q, *J* = 53.0 Hz), 77.72, 77.28, 26.69. ^{19}F NMR (470 MHz, $CDCl_3$) δ -50.23 (s, 3F).GC-MS (EI): m/z 212 (M^+).

*4.3.8 4-(3,3,3-trifluoroprop-1-yn-1-yl)benzonitrile (**2i**):*Yellow solid (42 mg, 54% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.69 (d, *J* = 8.5 Hz, 2H), 7.67 (d, *J* = 8.5 Hz, 2H).^{13}C NMR (126 MHz, $CDCl_3$) δ 131.99 (q, *J* = 1.3 Hz), 131.31, 122.14, 116.55, 113.43 (q, *J* = 258.3 Hz), 113.61, 83.00 (q, *J* = 6.5 Hz),77.88(q, *J* = 54.2 Hz). ^{19}F NMR (470 MHz, $CDCl_3$) δ -50.52 (s, 3F).GC-MS (EI): m/z 195 (M^+).

*4.3.9 1-Nitro-2-(3,3,3-trifluoroprop-1-yn-1-yl)benzene (**2j**):*Brown solid (43 mg, 50% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.1 Hz, 1H), 7.83-7.62 (m, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 149.83, 135.66, 133.50, 131.63, 125.15, 114.51 (q, *J* = 258.4 Hz), 114.14, 81.60 (q, *J* = 53.4 Hz), 81.54 (q, *J* = 6.7 Hz).^{19}F NMR (470 MHz, $CDCl_3$) δ -50.73 (s, 3F).GC-MS (EI): m/z 215 (M^+).

*4.3.10 1-Bromo-4-(3,3,3-trifluoroprop-1-yn-1-yl)benzene (**2k**):* Yellow oil (31 mg, 31% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 8.4 Hz, 2H).^{13}C NMR (126 MHz, $CDCl_3$) δ 133.75, 132.08, 125.73, 117.41 (q, *J* = 1.8 Hz), 114.72 (q, *J* = 257.0 Hz), 85.37 (q, *J* = 6.5 Hz) . ^{19}F NMR (470 MHz, $CDCl_3$) δ -50.06 (s, 3F).GC-MS (EI): m/z 248 (M^+).

*4.3.11 1-Chloro-4-(3,3,3-trifluoroprop-1-yn-1-yl)benzene (**2l**):* Yellow solid (33 mg, 40% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.6 Hz, 2H), 7.38 (d, *J* = 8.6 Hz, 2H).^{13}C NMR (126 MHz, $CDCl_3$) δ137.37 (s), 133.65 (d, *J* = 1.5 Hz), 129.15 (s), 116.94 (d, *J* = 1.8 Hz), 114.71 (q, *J* = 257.0 Hz), 85.31 (q, *J* = 6.4 Hz), 85.31 (q, *J* = 6.4 Hz), 76.65(q, *J* = 53.1 Hz). ^{19}F NMR (470 MHz, $CDCl_3$) δ -50.01 (s, 3F). GC-MS (EI): m/z 204 (M^+).

*4.3.12 1-Bromo-3-(3,3,3-trifluoroprop-1-yn-1-yl)benzene (**2m**):* Yellow oil (66 mg, 53% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (s, 1H), 7.61 (d, *J* = 8.1 Hz, 1H), 7.49 (d, *J* = 7.7 Hz, 1H), 7.27 (t, *J* = 7.9 Hz, 1H).^{13}C NMR (126 MHz, $CDCl_3$) δ 135.09 (q, *J* = 1.5 Hz), 134.14, 130.96 (q, *J* = 1.4 Hz), 130.11, 122.46, 120.44 (q, *J* = 1.8 Hz), 114.62 (q, *J* = 258.3 Hz), 84.63 (q, *J* = 6.5 Hz),76.66(q, *J* = 53.0 Hz) . ^{19}F NMR (470 MHz, $CDCl_3$) δ -50.16 (s, 3F). GC-MS (EI): m/z 248 (M^+).

*4.3.13 1-(3,3,3-trifluoroprop-1-yn-1-yl)naphthalene (**2n**):* Yellow oil (45 mg, 51% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.3 Hz, 1H), 7.93 (d, *J* = 8.3 Hz, 1H), 7.86 (d, *J* = 8.1 Hz, 1H), 7.78 (d, *J* = 7.2 Hz, 1H), 7.65 – 7.58 (m, 1H), 7.58 – 7.52 (m, 1H), 7.44 (dd, *J* = 10.6, 4.8 Hz, 1H).^{13}C NMR (126 MHz, $CDCl_3$) δ 133.16 (q, *J* = 0.8 Hz), 132.99, 132.52 (q, *J* = 1.8 Hz), 131.53, 128.59, 127.82, 127.03, 125.30, 124.98, 115.98 (q, *J* = 1.76 Hz), 115.10 (q, *J* = 258.3 Hz), 85.20 (q, *J* = 6.4 Hz), 80.18 (q, *J* = 52.9 Hz). ^{19}F NMR (470 MHz, $CDCl_3$) δ -49.42 (s, 3F). GC-MS (EI): m/z 220 (M^+).

*4.3.14 3-(3,3,3-trifluoroprop-1-yn-1-yl)quinoline (**2o**):* Yellow solid (54mg, 61%yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.86 (s, 1H), 8.29 (s, 1H), 8.04 (d, *J* = 8.8 Hz, 1H), 7.71 (t, *J* = 7.6 Hz, 2H), 7.53 (t, *J* = 7.5 Hz, 1H).^{13}C NMR (126 MHz, $CDCl_3$) δ 151.11, 147.93, 140.81 (q, *J* = 1.4 Hz), 131.65 (s), 129.64, 127.95, 127.92, 126.53, 115.65 (q, *J* = 257.0 Hz), 112.59 (q, *J* = 1.6 Hz), 83.87 (q, *J* = 6.4 Hz), 78.48 (q, *J* = 51.7 Hz). ^{19}F NMR (470 MHz, $CDCl_3$) δ -50.11(s, 3F). GC-MS (EI): m/z 221 (M^+).

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