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Domino Hydroboration/Trifluoromethylation of Alkynes Using Fluoroform-Derived $CuCF_3$

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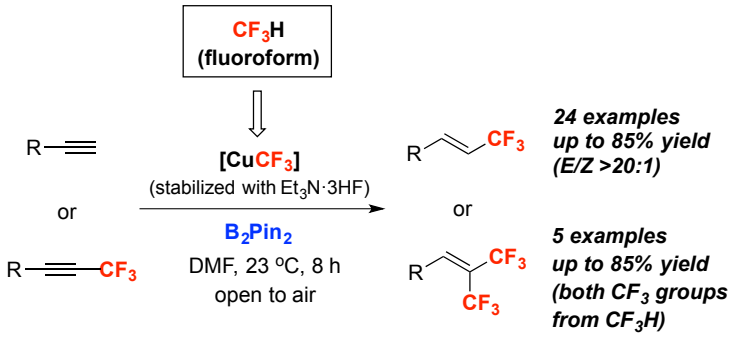
ABSTRACT

A domino hydroboration/trifluoromethylation (formal hydrotrifluoromethylation) of alkynes using the fluoroform-derived [$CuCF_3$] reagent is achieved. Synthetically useful (*E*)-alkenyl-CF_3 building blocks and 1,1-bis(trifluoromethyl)-substituted alkenes can be prepared under ambient conditions in one-pot/one-step from alkynes. The ultimate source of CF_3 is the inexpensive industrial waste fluoroform.



INTRODUCTION

The importance of organofluorine compounds in pharmaceuticals, agrochemicals and materials cannot be overstated.[1] In particular, the incorporation of trifluoromethyl (CF_3) groups can significantly enhance the bioavailability, metabolic stability,

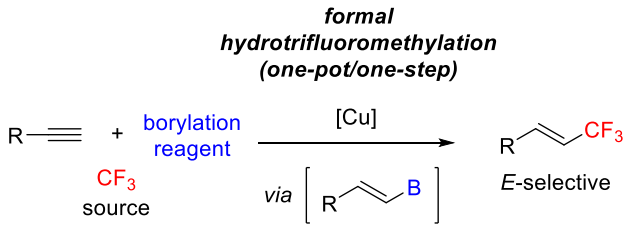
lipophilicity and binding selectivity of drug candidates.[2] Driven by its high demand, a surge of new trifluoromethylation methods can be witnessed in recent years.[3]

Compared to the formation of aryl-CF_3 bonds,[3g-i] the area of alkenyl-CF_3 bond formation is underdeveloped.[3i,4,5,7] Traditional approaches such as Horner or Julia–Kocienski olefination reactions generally provide *E*/*Z* mixtures of trifluoromethylated alkenes.[4] More modern approaches involve transition metal-catalyzed/-mediated cross-coupling reactions between alkenyl species and CF_3 sources.[5] The alkenyl coupling partners, including vinyl boronic acids,[5a-c] trifluoroborates,[5d-f] carboxylic acids,[5g-j] halides[5k-l] and sulfonates,[5m] are pre-functionalized substrates and usually tedious to synthesize. In most cases, electrophilic CF_3 sources, *e.g.* Togni[6a] and Umemoto[6b] reagents, were employed that were expensive or need to be prepared separately.[7] Direct trifluoromethylation of terminal alkenes have also been reported, however, the substrate scopes were rather limited to specialized alkenes.[8]

An alternative approach is the *hydrotrifluoromethylation* of terminal alkynes to obtain the trifluoromethylated alkenyl-CF_3 products.[9] Apart from an isolated early example of ultrasound-promoted reaction,[10a] only a handful of methods are available using photocatalytic,[10b-d] radical-mediated[10e] and metal-catalyzed[10f] reactions. They provided convenient access to trifluoromethylated alkenes but suffered universally from the problems of *E/Z* selectivities. Therefore, the search for an efficient, selective

and convenient method for synthesizing trifluoromethylated alkenes is still much needed. Inspired by the precedents of trifluoromethylation of vinyl boron species[5a-f] and Cu-mediated hydroboration of alkynes,[11] we envision that a *domino hydroboration/trifluoromethylation* process[12] (formal hydrotrifluoromethylation) can be developed to selectively construct the C(sp^2)-CF_3 bond in one-pot/one-step from terminal alkynes (Scheme 1).

Scheme 1. Synthesis of (*E*)-alkenyl-CF_3 products *via* copper-mediated domino hydroboration/trifluoromethylation of terminal alkynes

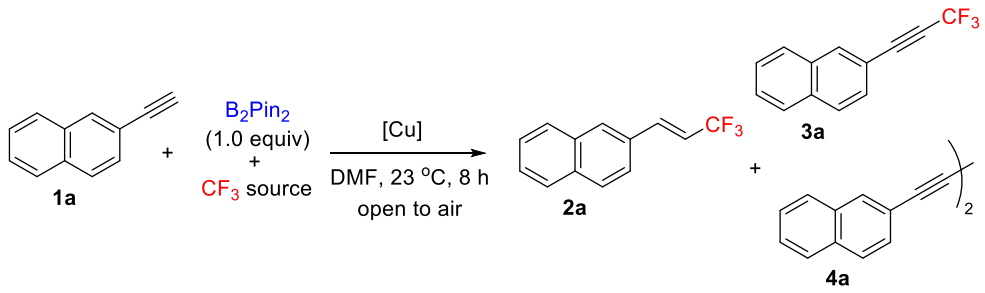


RESULTS AND DISCUSSION

We began the studies by identifying a suitable combination of CF_3 source and copper promoter, using 2-ethynylnaphthalene **1a** as the substrate and bis(pinacolato)diboron (B_2Pin_2)[11e-i] as the borylation reagent (Scheme 2). In the presence of CuCl under aerobic conditions, electrophilic Togni reagent[6a] and nucleophilic $TMSCF_3$[3c] were ineffective in forming the desired product **2a**, giving alkynyl-CF_3 **3a** and dimer **4a** instead as major side products (conditions A-B).[13] Adding proton sources such as MeOH or $Et_3N{\cdot}3HF$ also did not give the desired product **2a** in condition B. The copper complex $(PPh_3)_3CuCF_3$[14] gave 28% yield of **2a**

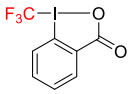
but a significant amount of dimer **4a** (condition C). To our delight, the fluoroform-derived [$CuCF_3$],[15] prepared by Grushin's method,[16a] provided a good yield (80%) of **2a** (*E/Z* >20:1) with minimum amounts of side products (condition D). Fluoroform (CF_3H, trifluoromethane, HFC-23) is an industrial byproduct from Teflon manufacturing and is commercially available at low cost. Grushin's pioneering work on the preparation and applications of fluoroform-derived [$CuCF_3$] is one of the most useful and practical approaches for utilizing fluoroform as a CF_3 source in organic synthesis.[16] We have also previously employed this reagent for efficient C(*sp*)-CF_3 and C(sp^3)-CF_3 bond formations with alkynes and alkenes.[17]

Scheme 2. Initial studies of CF_3 sources and copper promoter



CF_3 source and [Cu]:

A) Togni reagent (2.0 equiv), CuCl (2.0 equiv)
^{19}F NMR yields of **2a**/**3a**/**4a** = <5/35/-



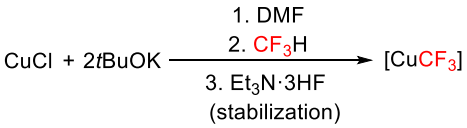
Togni reagent

B) $TMSCF_3$ (10 equiv), KF (10 equiv), CuCl (2.0 equiv)
^{19}F NMR yields of **2a**/**3a**/**4a** = <5/70/-

C) $(PPh_3)_3CuCF_3$ (2.0 equiv)
^{19}F NMR yields of **2a**/**3a**/**4a** = 28/-/60

D) Fluoroform-derived [$CuCF_3$] (2.0 equiv)
^{19}F NMR yields of 2a/3a/4a = 80/<5/7

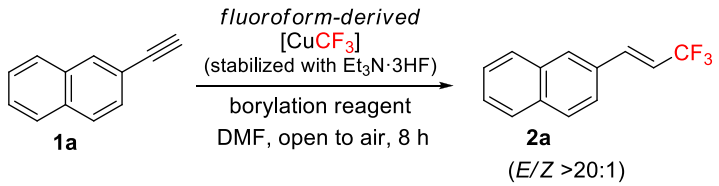
Preparation of fluoroform-derived [$CuCF_3$] by Grushin's method:



Encouraged by the promising initial results, we proceeded with the optimization studies (Table 1, see Supporting Information for full details). Using pinacolborane (HBPin) or without borylation reagent afforded only trace products (entries 1-2). Control experiment showed no conversion in the absence of [$CuCF_3$]. A slight excess (1.2 equiv) of B_2Pin_2 increased the yield but the yield was decreased with larger excess (entries 3-4). On the other hand, increasing the equivalents of [$CuCF_3$] (2.5 equiv) had no effect but less [$CuCF_3$] (1.5 equiv) caused a drop in yield (entry 5-6). Increasing the reaction temperature gave lower yields (entries 7-8). The highest yield of alkene **2a** (92%, 85% isolated, *E*/*Z* >20:1) was obtained with a lower concentration

(0.05M) (entry 9). The reaction was best run open to air, bubbling oxygen or using Ag_2CO_3 as an oxidant led to much poorer yields (entries 10-11).

Table 1. Optimization studies.[a]



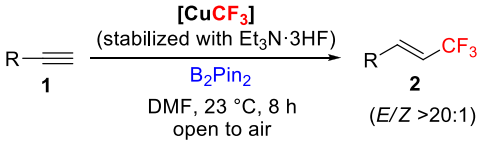
entry	equiv of [$CuCF_3$]	borylation reagent (equiv)	temp (^oC)	yield of **2a** (%)[b]
1	2.0	HBPin (1.0)	23	<5
2	2.0	none	23	<5
3	2.0	B_2Pin_2 (1.2)	23	89
4	2.0	B_2Pin_2 (2.0)	23	40
5	2.5	B_2Pin_2 (1.2)	23	89
6	1.5	B_2Pin_2 (1.2)	23	81
7	2.0	B_2Pin_2 (1.2)	35	85
8	2.0	B_2Pin_2 (1.2)	50	70
9[c]	**2.0**	**B_2Pin_2 (1.2)**	**23**	**92 (85)**[d]
10[e]	2.0	B_2Pin_2 (1.2)	23	23
11[f]	2.0	B_2Pin_2 (1.2)	23	21

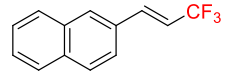
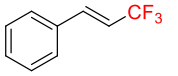
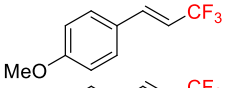
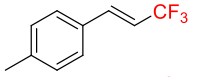
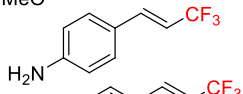
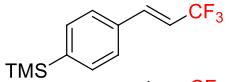
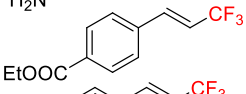
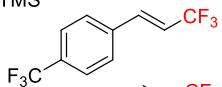
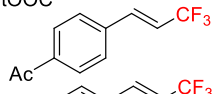
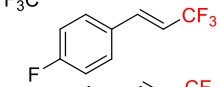
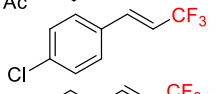
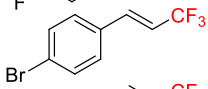
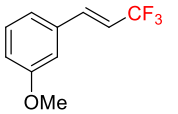
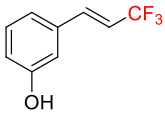
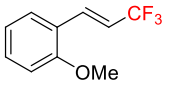
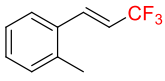
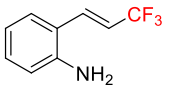
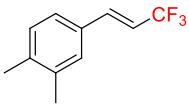
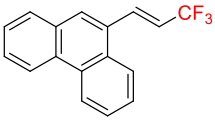
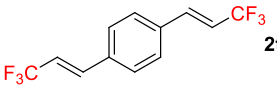
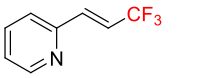
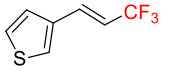
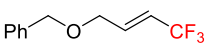
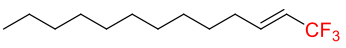
[a]General conditions: [$CuCF_3$] (in DMF solution, stabilized by $Et_3N{\cdot}3HF$) was added to a mixture of **1a** (0.1 mmol) and borylation reagent in DMF (1.0 mL). The [$CuCF_3$] was prepared from CuCl/*t*-BuOK/fluoroform according to Grushin's procedure in ref 16a. [b]Yield was determined by ^{19}F NMR analysis using fluorobenzene as the internal standard. [c]1.5 mL of DMF. [d]Isolated yield. [e]Oxygen was bubbled through the reaction mixture. [f]Reaction was under argon in the presence of Ag_2CO_3 (2.0 equiv).

With the optimized conditions in hand, we next investigated the scope of terminal alkynes **1** in this reaction (Table 2). A wide range of aryl-/heteroaryl-substituted alkenyl-CF_3 products (**2a-v**) were obtained in moderate to good yields with broad functional group compatibility. In general, electron-rich

aromatic alkynes gave higher yields (**2a-f** *vs.* **2g-i**). Substituents at the *para* (**2c-l**), *meta* (**2m-n**) and *ortho* (**2o-q**) positions of the aromatic ring were all tolerated. Bulkier aromatic (**2s**) and heteroaromatic groups (**2u-v**) were also compatible. The structurally intriguing bis-trifluoromethylated product **2t** could be obtained from the corresponding 1,4-diyne substrate using a larger excess of the reagents. The chemoselectivity of the reaction was remarkable as trifluoromethylation of arylsilanes[18] and aryl bromides[16a,e] with copper CF_3 reagents are known, and yet the aromatic silyl (**2f**) and halogen (**2j-l**) substituents remained intact under the reaction conditions. Moreover, sensitive groups such as the unprotected amino (**2e**,**q**) and hydroxy (**2n**) groups were also tolerated. The volatility of some products made the isolation difficult, therefore these reactions were carried out on a larger scale and NMR yields were given for comparison. Finally, alkyl-substituted products (**2w-x**) were obtained albeit in lower yields. Attempted optimization including changing the reaction temperature and equivalents of $CuCF_3$, prolonging reaction time and adding ligands did not improve the yield of **2x**. In all cases, the *E/Z* selectivity of the reaction was excellent (>20:1).

Table 2. Scope of terminal alkynes 1 in the synthesis of (*E*)-alkenyl-CF_3 products 2.[a]



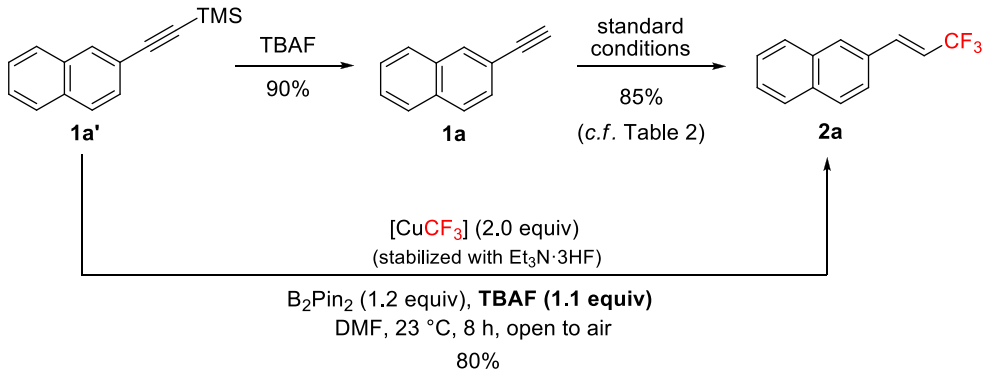
Product		Isolated Yield %	Product		Isolated Yield %
	**2a**	85, 80[b]		**2b**	52[b], 90[c]
	**2c**	82		**2d**	52[b], 88[c]
	**2e**	73		**2f**	83
	**2g**	52		**2h**	30
	**2i**	51		**2j**	60[b], 90[c]
	**2k**	83		**2l**	70
	**2m**	80		**2n**	70
	**2o**	78		**2p**	60[b], 85[c]
	**2q**	65		**2r**	65[b], 85[c]
	**2s**	83		**2t**	75[d]
	**2u**	30[b], 50[c]		**2v**	40[b], 90[c]
	**2w**	43		**2x**	35

[a]General conditions: [$CuCF_3$] (in DMF solution, 2.0 equiv, prepared from CuCl/*t*-BuOK/fluoroform, stabilized by $Et_3N{\cdot}3HF$) was added to the mixture of **1** (0.2 mmol) and B_2Pin_2 (1.2 equiv) in DMF (3.0 mL). [b]1 mmol scale. [c]Yield was determined by ^{19}F NMR analysis using fluorobenzene as the internal standard. [d]4.0 equiv of [$CuCF_3$] and 2.4 equiv of B_2Pin_2.

Some of the terminal alkynes such as **1a** were prepared from the TMS-protected alkynes by desilylation. We envisioned that a one-pot/one-step desilylation/hydroboration/trifluoro-methylation of TMS-protected alkyne **1a'** was

possible (Scheme 3). Indeed, the one-pot protocol was equally efficient as the two-step sequence (80% yield *vs.* 77% yield over two steps), using extra tetrabutylammonium fluoride (TBAF), but without the separation and purification of **1a.**

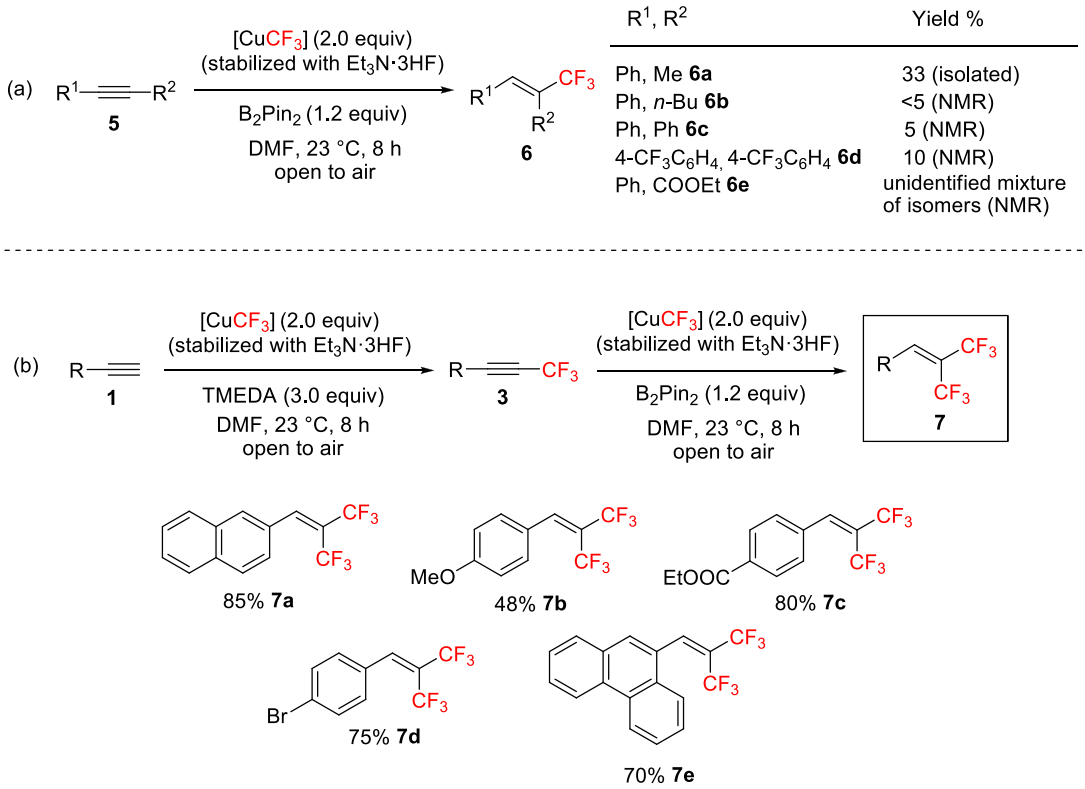
Scheme 3. One-pot synthesis of 2a from TMS-protected alkyne 1a'



When applying the reaction to internal alkynes **5**, we encountered low conversions and yields (Scheme 4a). We were able to isolate 33% yield of the phenyl/methyl-substituted alkenyl product (*E*)-**6a**. However, reactivity decreased sharply with alkynes containing bulkier phenyl/*n*-butyl (**5b**) and phenyl/phenyl (**5c**) substituents. On the other hand, an electron-withdrawing group such as 4-CF_3 on the phenyl ring improved the yield to a certain extent (**6c** *vs.* **6d**). Conversion improved significantly in the case of internal alkyne having an electron-withdrawing group such as COOEt (**5e**). However, an unidentified mixture of isomers (regio- and/or stereo-) was observed. These results pointed to the probable tolerance of a small and electron-deficient substituent group on the internal alkyne. Indeed, the CF_3-containing

internal alkynes **3** were suitable substrates for the reaction, which can be prepared conveniently from terminal alkynes **1** by our previously reported trifluoromethylation method using fluoroform-derived [$CuCF_3$] (Scheme 4b).[17a] A variety of 1,1-bis(trifluoromethyl)-substituted alkenyl products **7a-e** were synthesized from **3** in moderate to good yields. The steric bias of the alkyne substituents (aryl *vs.* CF_3) could account for the high regioselectivity.[20,21] The preparation of these potentially useful fluorinated building blocks have only been described by a handful of early reports using indirect approaches.[22] Our method offered an easy access to **7** in only two steps from readily available terminal alkynes **1** and notably the source of *both* CF_3 groups was fluoroform.

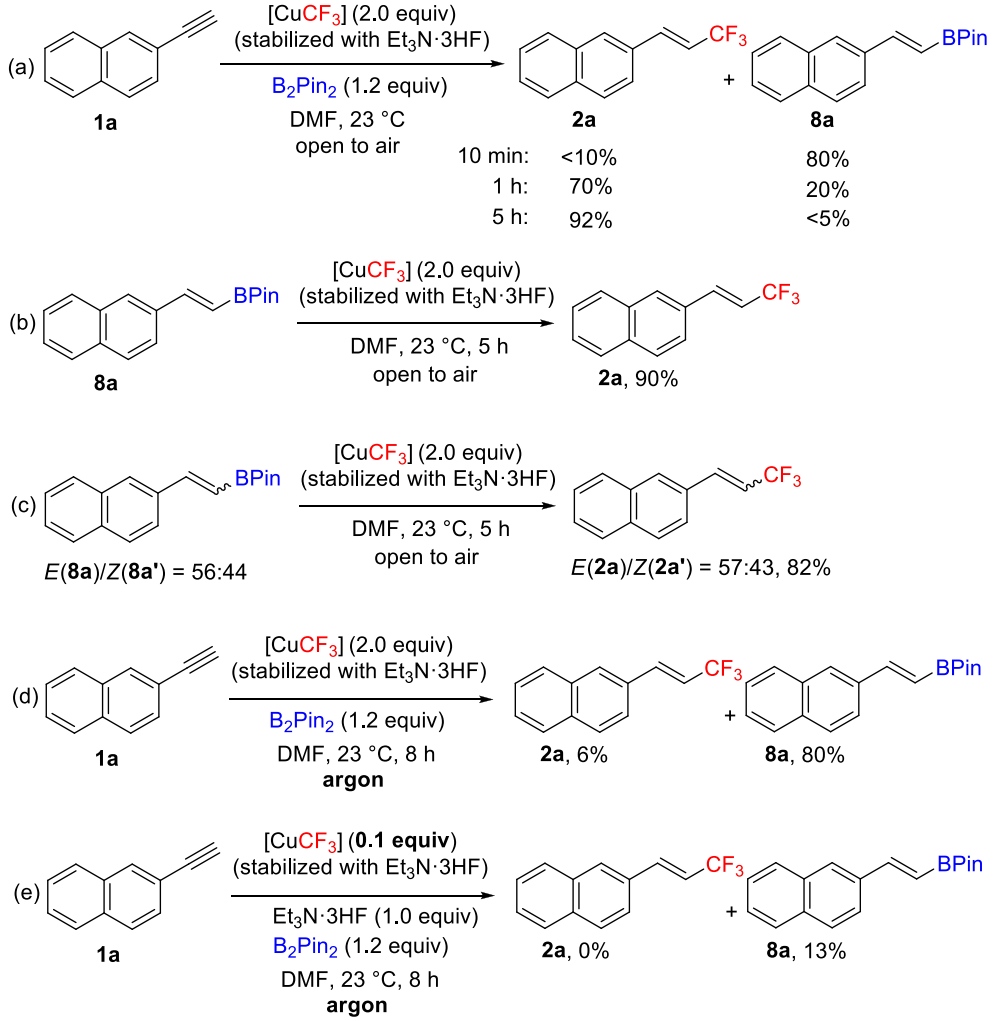
Scheme 4. (a) Using Internal Alkynes as substrates. (b) Synthesis of 1,1-Bis(trifluoromethyl)-Substituted Alkenes 7 using CF_3-Containing Internal Alkynes 3.



A series of experiments were conducted to gain mechanistic insights (Scheme 5). We were able to intercept the (*E*)-vinyl BPin intermediate **8a** in 80% yield after 10 min reaction time. Prolonged reaction time led to the expected alkenyl-CF_3 product **2a** (Scheme 5a). This (*E*)-vinyl BPin **8a** participated in the trifluoromethylation reaction smoothly using fluoroform-derived [$CuCF_3$] to provide (*E*)-**2a** (Scheme 5b). The *E/Z* (56:44) mixture of **8a** and **8a'** gave the *E/Z* mixture of **2a** and **2a'** in similar ratio (57:43) under identical conditions (Scheme 5c). When the reaction was carried out under argon, the major product obtained from **1a** was the vinyl BPin **8a** instead

(Scheme 5d). When using a catalytic amount of [$CuCF_3$] (0.1 equiv), only 13% of **8a** was obtained with low conversion of **1a** (Scheme 5e).

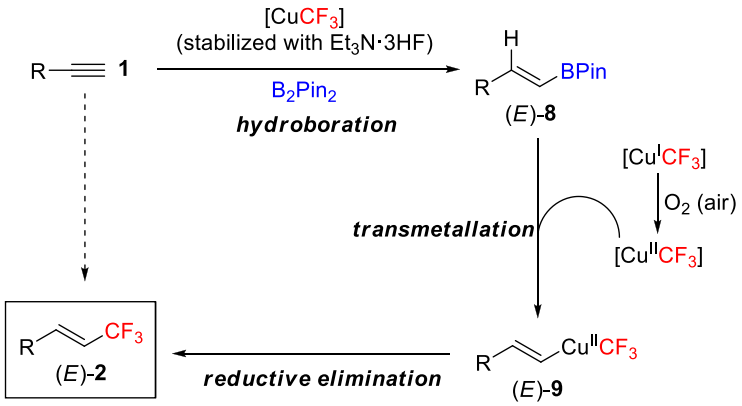
Scheme 5. Mechanistic Studies



Based on these studies and known literature examples, we propose the following reaction mechanism for the domino hydroboration/trifluoromethylation of terminal alkynes using the fluoroform-derived [$CuCF_3$] (Scheme 6). In the presence of B_2Pin_2, the initial [Cu^ICF_3] presumably generates a borylcopper species for the regio- and stereoselective hydroboration of terminal alkyne **1** to form (*E*)-vinyl BPin **8**. This process can occur *via* *anti*-Markovnikov *syn*-borylcupration and subsequent

protonation thus accounting for the high levels of regio- and stereo-control.[11e-g,19,20] An excess amount of the unstable [$Cu^{I}CF_3$][16a,17a] is needed for the efficient hydroboration (*c.f.* Scheme 5d-e). The stabilizer $Et_3N{\cdot}3HF$ also plays the role as the proton source. The [$Cu^{I}CF_3$] species can be oxidized to [$Cu^{II}CF_3$][16b] in air, which is needed for transmetallation to form the (*E*)-vinyl $CuCF_3$ species **9**. The exact nature of this species is unclear, however, the involvement of [$Cu^{III}CF_3$] cannot be completely ruled out.[23] The final reductive elimination leads to the (*E*)-alkenyl CF_3 product **2**. Overall, the (*E*)-selective hydrotrifluoromethylation of terminal alkynes **1** is achieved.

Scheme 6. Proposed Mechanism



CONCLUSION

In summary, we have developed a new synthetic method for the preparation of useful (*E*)-alkenyl-CF_3 building blocks **2** and 1,1-bis(trifluoromethyl)-substituted alkenes **7** using the fluoroform-derived [$CuCF_3$] reagent. The reaction has the following unique features: (1) converting easily accessible terminal alkynes into

alkenyl-CF_3 products with excellent *E*-selectivity and good functional group tolerance; (2) utilizing a domino hydroboration/trifluoromethylation sequence in one-pot/one-step without the isolation of intermediates; (3) mild reaction conditions at room temperature and open to air; (4) using the inexpensive industrial waste fluoroform as the CF_3 source.

EXPERIMENTAL SECTION

General Experimental. Unless otherwise noted, the hydrotrifluoromethylation reactions were carried out open to air in a test tube or round bottom flask (RBF) with magnetic stirring. Analytical thin layer chromatography (TLC) was performed with EM Science silica gel 60 F254 aluminum plates. Visualization was done under a UV lamp (254 nm) and by immersion in ethanolic phosphomolybdic acid (PMA) or potassium permanganate ($KMnO_4$), followed by heating using a heat gun. Organic solutions were concentrated by rotary evaporation at 23–35 °C. Purification of reaction products was generally done by flash column chromatography with Grace Materials Technologies 230−400 mesh silica gel. It should be noted that most of the hydrotrifluoromethylated products **2** are volatile and therefore high vacuum should be avoided.

Materials. Fluoroform (Research Grade, Purity: 99.999% min., 9.1kg in 16 L size cylinder) was purchased from SynQuest Laboratories, USA. Copper (I) chloride

(extra pure, 99.99%) and $Et_3N{\cdot}3HF$ (97%) were purchased from Acros. Potassium *tert*-butoxide (97%) was purchased from Alfa Aesar. B_2Pin_2 was purchased from J&K Scientific. DMF was dried over solvent purification system, stored over *4Å molecular sieves* and degassed before use. Other reagents were purchased from Acros, J&K Scientific and Aldrich. Alkynes **1b**,**d**,**h**,**j**,**p**,**u**,**v,x** and **5a**,**b**,**c** were purchased from commercial sources. Other alkynes and the (*E)*-vinyl BPin **8a** were known compounds and prepared according to literature procedures.[24]

Instrumentation. Proton nuclear magnetic resonance spectra (^{1}H NMR) spectra, carbon nuclear magnetic resonance spectra (^{13}C NMR) and fluorine nuclear magnetic resonance spectra (^{19}F NMR) were recorded at 23 °C on a Bruker 400 spectrometer in $CDCl_3$ (400 MHz for ^{1}H and 100 MHz for ^{13}C and 376 MHz for ^{19}F). Chemical shifts for protons were reported as parts per million in δ scale using solvent residual peak ($CHCl_3$: 7.26 ppm) as internal standards. Chemical shifts of ^{13}C NMR spectra were reported in ppm from the central peak of $CDCl_3$ (77.16 ppm) on the δ scale. Chemical shifts of ^{19}F NMR are reported as parts per million in δ scale using fluorobenzene (-113.15 ppm) as internal standards. Data are represented as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintuplet, oct = octuplet, m = multiplet, br = broad), and coupling constant (*J*, Hz). Infrared spectra were recorded on a Nicolet 420 FT-IR spectrophotometer and

reported in wave numbers (cm^{-1}).High resolution mass spectra (HRMS) were obtained on a Finnigan MAT 95XL GC Mass Spectrometer with the mass analyzer of magnetic sector used.

Experimental Procedures.

Procedures for the preparation of fluoroform-derived $CuCF_3$ reagent: [16a,17a]

In a glove box, to a 50 mL RBF was charged CuCl (0.50 g, 5.05 mmol), *t*-BuOK (1.18 g, 10.54 mmol) and a stir bar. The flask was sealed with a septum, brought out of the glove box and put under an argon atmosphere. Degassed DMF (11 mL) was added *via* syringe and the mixture was stirred at room temperature for 30 min. The flask was then evacuated on a vacuum line for 10 seconds (the weight of the whole flask was obtained). Then fluoroform was quickly bubbled into the mixture by using a needle connected to the fluoroform cylinder or a fluoroform balloon at room temperature for 5 min. After removing the fluoroform inlet, the weight of the whole flask was obtained again, and the amount of fluoroform in the flask was calculated (~1.1 g, ~15 mmol). The mixture was stirred for 5 min and $Et_3N{\cdot}3HF$ (0.43 mL, 2.65 mmol) was added under argon and the mixture was stirred for another 5 min. A colorless/slightly brown solution with some white solid was obtained as the $[Cu^{I}CF_3]$ solution in DMF (~0.4 M). The yield of $[Cu^{I}CF_3]$ was generally >90% determined by ^{19}F NMR analysis (DMF, unlocked) using fluorobenzene as the internal standard.

General procedure for the synthesis of (*E*)-alkenyl-CF_3 products 2 with fluoroform-derived $CuCF_3$ and B_2Pin_2 (Table 1−2, Scheme 2 Condition D, Scheme 4): Alkynes (**1**, **3** or **5**, 0.2 mmol, 1.0 equiv.), B_2Pin_2 (0.24 mmol, 1.2 equiv.) and DMF (3 mL) were added to a 10 mL RBF with a magnetic stir bar. Then the flask was sealed with a septa and flushed with argon. Fluoroform-derived $CuCF_3$ (0.4 M in DMF, 1.0 mL, 2.0 equiv.) was then added under argon. Then the septa was removed and the mixture was stirred in air at room temperature for 8 h. The reaction mixture turned dark brown when adding the $CuCF_3$ and some black solid formed in a few minutes, and then the solid slowly dissolved during the reaction. The reaction mixture was filtered through a short pad of silica gel and rinsed with 30% diethyl ether in hexanes (100 mL) and then concentrated by rotary evaporator. The crude mixture was purified by flash column chromatography on silica gel.

2a: *(E)-2-(3,3,3-trifluoroprop-1-en-1-yl)naphthalene.* Prepared according to the general procedure and purified by flash column chromatography (hexane). White solid; 38 mg, 85% (0.2 mmol scale); 176 mg, 80% (1 mmol scale). R_f = 0.55 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87–7.84 (m, 4H), 7.60 (dd, $J_{H\text{-}H}$= 8.7, 1.5 Hz, 1H), 7.55–7.51 (m, 2H), 7.32 (dq, $J_{H\text{-}H}$ = 16.1 Hz, $J_{H\text{-}F}$ = 2.1 Hz, 1H), 6.32 (dq, $J_{H\text{-}H}$ = 16.1 Hz, $J_{H\text{-}F}$ = 6.5 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.9 (q, $J_{C\text{-}F}$ = 6.8 Hz), 134.2, 133.4, 131.0, 129.2, 128.9, 128.6, 127.9, 127.3, 126.9, 123.9 (q, $J_{C\text{-}F}$ = 268.9 Hz),

123.3, 116.1 (q, J_{C-F} = 33.8 Hz) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ -63.2 (dd, J_{H-F} = 6.5, 2.0 Hz, 3F) ppm. The spectral data are in accordance with the literature report.[16i]

2b: *(E)-(3,3,3-trifluoroprop-1-en-1-yl)benzene.* Prepared according to the general procedure and purified by flash column chromatography (pentane). Colorless oil, 90 mg, 52% (1 mmol scale). R_f = 0.72 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48–7.39 (m, 5H), 7.17 (dq, J_{H-H} = 16.1 Hz, J_{H-F} = 2.2 Hz, 1H), 6.22 (dq, J_{H-H} = 16.1 Hz, J_{H-F} = 6.5 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.8 (q, J_{C-F} = 6.8 Hz), 133.6, 130.2, 129.1, 127.7, 123.8 (q, J_{C-F} = 268.7 Hz), 116.0 (q, J_{C-F} = 33.8 Hz) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ -63.4 (dd, J_{H-F} = 6.6, 2.2 Hz, 3F) ppm. The spectral data are in accordance with the literature report.[25]

2c: *(E)-1-methoxy-4-(3,3,3-trifluoroprop-1-en-1-yl)benzene.* Prepared according to the general procedure and purified by flash column chromatography (5% EtOAc/hexane). White solid; 33 mg, 82%. R_f = 0.65 (10% EtOAc/hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (d, J_{H-H} = 8.8 Hz, 2H), 7.09 (dq, J_{H-H} = 16.1 Hz, J_{H-F} = 2.1 Hz, 1H), 6.91 (d, J = 8.8 Hz, 2H), 6.07 (dq, J_{H-H} = 16.1 Hz, J_{H-F} = 6.6 Hz, 1H), 3.84 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.2, 137.2 (q, J_{C-F} = 6.8 Hz), 129.2, 126.2, 124.1 (q, J_{C-F} = 268.5 Hz), 114.5, 113.5 (q, J_{C-F} = 33.6 Hz), 55.5 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ -62.9 (dd, J_{H-F} = 6.6, 2.0 Hz, 3F) ppm. The spectral data are in accordance with the literature report.[22]

2d: *(E)-1-methyl-4-(3,3,3-trifluoroprop-1-en-1-yl)benzene.* Prepared according to the general procedure and purified by flash column chromatography (pentane). White solid; 117 mg, 63% (1 mmol scale). R_f = 0.75 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (d, J_{H-H} = 8.8 Hz, 2H), 7.21 (d, J_{H-H} = 8.8 Hz, 2H), 7.14 (dq, J_{H-H} = 16.1 Hz, J_{H-F} = 2.0 Hz, 1H), 6.17 (dq, J_{H-H} = 16.1 Hz, J_{H-F} = 6.6 Hz, 1H), 2.40 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.5, 137.7 (q, J_{C-F} = 6.8 Hz), 130.8, 129.8, 127.6, 124.0 (q, J_{C-F} = 268.7 Hz), 114.9 (q, J_{C-F} = 33.7 Hz), 21.5 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ -63.2 (d, J_{H-F} = 6.7 Hz, 3F) ppm. The spectral data are in accordance with the literature report.[5j]

2e: *(E)-4-(3,3,3-trifluoroprop-1-en-1-yl)aniline.* Prepared according to the general procedure and purified by flash column chromatography (15% EtOAc/hexane). Light brown solid, 27 mg, 73%. R_f = 0.48 (20% EtOAc/hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26 (d, J_{H-H} = 8.4 Hz, 2H), 7.02 (dq, J_{H-H} = 16.1 Hz, J_{H-F} = 2.1 Hz, 1H), 6.66 (d, J_{H-H} = 8.4 Hz, 2H), 5.98 (dq, J_{H-H} = 16.1 Hz, J_{H-F} = 6.7 Hz, 1H), 3.88 (brs, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.3, 137.6 (q, J_{C-F} = 6.8 Hz), 129.2, 124.3 (q, J_{C-F} = 268.2 Hz), 123.8, 115.1, 111.7 (q, J_{C-F} = 33.6 Hz) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ -62.5 (d, J_{H-F} = 6.7 Hz, 3F) ppm. The spectral data are in accordance with the literature report.[5j]

2f: *(E)-trimethyl(4-(3,3,3-trifluoroprop-1-en-1-yl)phenyl)silane.* Prepared according

to the general procedure and purified by flash column chromatography (hexane). Colorless oil, 40.5 mg, 83%. R_f = 0.70 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (d, J_{H-H} = 8.0 Hz, 2H), 7.43 (d, J_{H-H} = 8.0 Hz, 2H), 7.15 (dq, J_{H-H} = 16.1 Hz, J_{H-F} = 2.1 Hz, 1H), 6.23 (dq, J_{H-H} = 16.1 Hz, J_{H-F} = 6.5 Hz, 1H), 0.28 (s, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.4, 137.8 (q, J_{C-F} = 6.6 Hz), 134.0, 133.8, 126.8, 123.8 (q, J_{C-F} = 268.8 Hz), 116.1 (q, J_{C-F} = 33.8 Hz), -1.1 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ -63.4 (d, J_{H-F} = 6.8 Hz, 3F) ppm. IR (neat): 2957, 1665, 1271(br), 1124, 972, 842 cm^{-1}. HRMS m/z (EI): calcd. for $C_{12}H_{15}F_3Si$ $[M]^+$: 244.0890; found: 244.0891.

2g: *ethyl (E)-4-(3,3,3-trifluoroprop-1-en-1-yl)benzoate.* Prepared according to the general procedure and purified by flash column chromatography (5% EtOAc/hexane). Colorless oil, 25 mg, 52%. R_f = 0.52 (10% EtOAc/hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, J_{H-H} = 8.3 Hz, 2H), 7.51 (d, J_{H-H} = 8.3 Hz, 2H), 7.18 (dq, J_{H-H} = 16.2 Hz, J_{H-F} = 2.0 Hz, 1H), 6.30 (dq, J_{H-H} = 16.1 Hz, J_{H-F} = 6.4 Hz, 1H), 4.39 (q, J_{H-H} = 7.1 Hz, 2H), 1.40 (t, J_{H-H} = 7.1 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.1, 137.6, 136.8 (q, J_{C-F} = 6.8 Hz), 131.8, 130.3, 127.6, 123.4 (q, J_{C-F} = 269.1 Hz), 118.2 (q, J_{C-F} = 34.1 Hz), 61.4, 14.4 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ -63.7 (d, J_{H-F} = 6.4 Hz, 3F) ppm. The spectral data are in accordance with the literature report.[26]

2h: *(E)-1-(trifluoromethyl)-4-(3,3,3-trifluoroprop-1-en-1-yl)benzene.* Prepared according to the general procedure and purified by flash column chromatography

(pentane). Colorless oil, 72 mg, 30% (1 mmol scale). R_f = 0.73 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, J_{H-H} = 8.3 Hz, 2H), 7.57 (d, J_{H-H} = 8.3 Hz, 2H), 7.19 (dq, J_{H-H} = 16.2 Hz, J_{H-F} = 2.0 Hz, 1H), 6.30 (dq, J_{H-H} = 16.2 Hz, J_{H-F} = 6.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.9, 136.4 (q, J_{C-F} = 6.8 Hz), 131.9 (q, J_{C-F} = 32.7 Hz), 127.9, 126.1 (q, J_{C-F} = 3.8 Hz), 123.9 (q, J_{C-F} = 272.2 Hz), 123.3 (q, J_{C-F} = 269.2 Hz), 118.6 (q, J_{C-F} = 34.2 Hz) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ -62.9 (s, 3F), -63.8 (d, J_{H-F} = 6.4 Hz, 3F) ppm. The spectral data are in accordance with the literature report.[5e]

2i: *(E)-1-(4-(3,3,3-trifluoroprop-1-en-1-yl)phenyl)ethan-1-one.* Prepared according to the general procedure and purified by flash column chromatography (5% EtOAc/hexane). White solid, 21.5 mg, 51% R_f = 0.45 (10% EtOAc/hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, J_{H-H} = 8.3 Hz, 2H), 7.55 (d, J_{H-H} = 8.3 Hz, 2H), 7.19 (dq, J_{H-H} = 16.2 Hz, J_{H-F} = 2.0 Hz, 1H), 6.31 (dq, J_{H-H} = 16.2 Hz, J_{H-F} = 6.4 Hz, 1H), 2.62 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.4, 138.1, 137.8, 136.7 (q, J_{C-F} = 6.7 Hz), 129.1, 127.9, 123.4 (q, J_{C-F} = 269.2 Hz), 118.5 (q, J_{C-F} = 34.1 Hz), 26.8 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ -63.7 (dd, J_{H-F} = 6.5, 2.0 Hz, 3F) ppm. The spectral data are in accordance with the literature report.[5f]

2j: *(E)-1-fluoro-4-(3,3,3-trifluoroprop-1-en-1-yl)benzene.* Prepared according to the general procedure and purified by flash column chromatography (pentane), containing 4% of inseparable side product 4-fluorostyrene. Colorless oil, 114 mg, 60% (1 mmol

scale). R_f = 0.70 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46–7.43 (m, 2H), 7.14–7.07 (m, 3H), 6.13 (dq, J_{H-H} = 16.1 Hz, J_{H-F} = 6.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.9 (d, J_{C-F} = 250.5 Hz), 136.6 (q, J_{C-F} = 6.8 Hz), 129.8 (d, J_{C-F} = 3.2 Hz), 129.5 (d, J_{C-F} = 8.5 Hz), 123.7 (q, J_{C-F} = 268.8 Hz), 116.2 (d, J_{C-F} = 21.9 Hz), 115.8 (q, J_{C-F} = 34.1 Hz) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ -63.4 (dd, J_{H-F} = 6.4, 2.0 Hz, 3F), -110.3 (m, 1F) ppm. The spectral data are in accordance with the literature report.[5g]

2k: *(E)-1-chloro-4-(3,3,3-trifluoroprop-1-en-1-yl)benzene.* Prepared according to the general procedure and purified by flash column chromatography (pentane). Colorless oil, 34 mg, 83%. R_f = 0.74 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46−7.31 (m, 4H), 7.11 (dq, J_{H-H} = 16.2 Hz, J_{H-F} = 2.1 Hz, 1H), 6.18 (dq, J_{H-H} = 16.2 Hz, J_{H-F} = 6.5 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.6 (q, J_{C-F} = 6.8 Hz), 136.1, 132.0, 129.4, 128.9, 123.6 (q, J_{C-F} = 268.9 Hz), 116.6 (q, J_{C-F} = 34.1 Hz) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ -63.5 (d, J_{H-F} = 6.8 Hz, 3F) ppm. The spectral data are in accordance with the literature report.[5g]

2l: *(E)-1-bromo-4-(3,3,3-trifluoroprop-1-en-1-yl)benzene.* Prepared according to the general procedure and purified by flash column chromatography (hexane). White solid, 35 mg, 70%. R_f = 0.65 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (d, J_{H-H} = 8.4 Hz, 2H), 7.32 (d, J_{H-H} = 8.4 Hz, 2H), 7.09 (dq, J_{H-H} = 16.1 Hz, J_{H-F} = 1.9 Hz, 1H), 6.20 (dq, J_{H-H} = 16.1 Hz, J_{H-F} = 6.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ

136.6 (q, J_{C-F} = 6.8 Hz), 132.5, 132.3, 129.1, 124.4, 123.5 (q, J_{C-F} = 269.0 Hz), 116.7 (q, J_{C-F} = 34.1 Hz) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ -63.5 (d, J_{H-F} = 6.5 Hz, 3F) ppm. The spectral data are in accordance with the literature report.[5g]

2m: *(E)-1-methoxy-3-(3,3,3-trifluoroprop-1-en-1-yl)benzene.* Prepared according to the general procedure and purified by flash column chromatography (5% EtOAc/hexane). Pale-yellow oil, 32 mg, 80%. R_f = 0.62 (10% EtOAc/hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (t, J_{H-H} = 7.9 Hz, 1H), 7.12 (dq, J_{H-H} = 16.1 Hz, J_{H-F} = 2.0 Hz, 1H), 7.05 (d, J_{H-H} = 7.7 Hz, 1H), 6.97 (s, 1H), 6.93 (dd, J_{H-H} = 8.2, 2.2 Hz, 1H), 6.20 (dq, J_{H-H} = 16.1 Hz, J_{H-F} = 6.5 Hz, 1H), 3.84 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.1, 137.7 (q, J_{C-F} = 6.9 Hz), 134.9, 130.1, 123.7 (q, J_{C-F} = 269.0 Hz), 120.3, 116.3 (q, J_{C-F} = 33.8 Hz), 115.8, 112.9, 55.5 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ -63.4 (dd, J_{H-F} = 6.8, 2.2 Hz, 3F) ppm. The spectral data are in accordance with the literature report.[25]

2n: *(E)-3-(3,3,3-trifluoroprop-1-en-1-yl)phenol.* Prepared according to the general procedure and purified by flash column chromatography (15% EtOAc/hexane). Brown oil, 26 mg, 70%. R_f = 0.48 (20% EtOAc/hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26 (t, J_{H-H} = 7.9 Hz, 1H), 7.09 (dq, J_{H-H} = 16.1 Hz, J_{H-F} = 2.1 Hz, 1H), 7.03 (d, J_{H-H} = 7.7 Hz, 1H), 6.93 (s, 1H), 6.85 (dd, J_{H-H} = 8.0, 2.3 Hz, 1H), 6.17 (dq, J_{H-H} = 16.1 Hz, J_{H-F} = 6.5 Hz, 1H), 5.02 (brs, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.1, 137.4 (q,

$J_{C\text{-}F}$ = 6.7 Hz), 135.2, 130.3, 123.7 (q, $J_{C\text{-}F}$ = 269.1 Hz), 120.5, 117.8, 116.5 (q, $J_{C\text{-}F}$ = 34.0 Hz), 114.1 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ -63.5 (d, $J_{H\text{-}F}$ = 7.0 Hz, 3F) ppm. The spectral data are in accordance with the literature report.[5j]

2o: *(E)-1-methoxy-2-(3,3,3-trifluoroprop-1-en-1-yl)benzene.* Prepared according to the general procedure and purified by flash column chromatography (5% EtOAc/hexane). Pale-yellow oil, 31 mg, 78%. R_f = 0.60 (10% EtOAc/hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45−7.41 (m, 2H), 7.37−7.33 (m, 1H), 6.97 (t, $J_{H\text{-}H}$ = 7.5 Hz, 1H), 6.93 (d, $J_{H\text{-}H}$ = 8.3 Hz, 1H), 6.34 (dq, $J_{H\text{-}H}$ = 16.3 Hz, $J_{H\text{-}F}$ = 6.6 Hz, 1H), 3.89 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.1, 133.2 (q, $J_{C\text{-}F}$ = 7.0 Hz), 131.3, 128.8, 124.1 (q, $J_{C\text{-}F}$ = 269.1 Hz), 122.5, 120.9, 116.6 (q, $J_{C\text{-}F}$ = 33.3 Hz), 111.2, 55.6 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ -63.3 (dd, $J_{H\text{-}F}$ = 6.6, 2.0 Hz, 3F) ppm. The spectral data are in accordance with the literature report.[5j]

2p: *(E)-1-methyl-2-(3,3,3-trifluoroprop-1-en-1-yl)benzene.* Prepared according to the general procedure and purified by flash column chromatography (pentane). Colorless oil, 112 mg, 60% (1 mmol scale). R_f = 0.75 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49−7.42 (m, 2H), 7.33−7.29 (m, 1H), 7.27−7.23 (m, 2H), 6.13 (dq, $J_{H\text{-}H}$ = 16.0 Hz, $J_{H\text{-}F}$ = 6.5 Hz, 1H), 2.42 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.1, 135.6 (q, $J_{C\text{-}F}$ = 6.7 Hz), 132.7, 130.9, 129.9, 126.6, 126.3, 123.7 (q, $J_{C\text{-}F}$ = 269.4 Hz), 117.2 (q, $J_{C\text{-}F}$ = 33.5 Hz), 19.7 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ -63.4 (dd, $J_{H\text{-}F}$ = 6.6, 2.1 Hz,

3F) ppm. The spectral data are in accordance with the literature report.[25]

2q: *(E)-2-(3,3,3-trifluoroprop-1-en-1-yl)aniline.* Prepared according to the general procedure and purified by flash column chromatography (10% EtOAc/hexane). Light brown solid, 24 mg, 65%. R_f = 0.65 (20% EtOAc/hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30−7.23 (m, 2H), 7.18 (t, J_{H-H} = 7.5 Hz, 1H), 6.80 (t, J_{H-H} = 7.5 Hz, 1H), 6.72 (d, J_{H-H} = 8.0 Hz, 1H), 6.13 (dq, J_{H-H} = 16.0 Hz, J_{H-F} = 6.5 Hz, 1H), 3.82 (brs, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.9, 133.5 (q, J_{C-F} = 6.7 Hz), 131.1, 128.1, 123.8 (q, J_{C-F} = 268.8 Hz), 119.6, 119.4, 116.9, 116.8 (q, J_{C-F} = 33.7 Hz) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ -63.2 (d, J_{H-F} = 6.5 Hz, 3F) ppm. The spectral data are in accordance with the literature report.[25]

2r: *(E)-1,2-dimethyl-4-(3,3,3-trifluoroprop-1-en-1-yl)benzene.* Prepared according to the general procedure and purified by flash column chromatography (pentane). Pale-yellow oil, 130 mg, 65% (1 mmol scale). R_f = 0.70 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20−7.11 (m, 3H), 7.07 (dq, J_{H-H} = 16.1 Hz, J_{F-H} = 2.2 Hz, 1H), 6.13 (dq, J_{H-H} = 16.1 Hz, J_{H-F} = 6.6 Hz, 1H), 2.26 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.2, 137.8 (q, J_{C-F} = 6.7 Hz), 137.3, 131.2, 130.3, 128.9, 125.2, 124.0 (q, J_{C-F} = 268.5 Hz), 114.6 (q, J_{C-F} = 33.6 Hz), 19.8, 19.8 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ -63.1 (d, J_{H-F} = 6.4 Hz, 3F) ppm. The spectral data are in accordance with the literature report.[5i]

2s: *(E)-9-(3,3,3-trifluoroprop-1-en-1-yl)phenanthrene.* Prepared according to the

general procedure and purified by flash column chromatography (hexane). White solid, 45 mg, 83%. R_f = 0.48 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.75 (d, J_{H-H}= 8.2 Hz, 1H), 8.68 (d, J_{H-H}= 8.2 Hz, 1H), 8.07 (d, J_{H-H}= 7.8 Hz, 1H), 7.96 (dq, J_{H-H} = 16.1 Hz, J_{H-F} = 1.9 Hz, 1H), 7.92 (d, J_{H-H}= 7.6 Hz, 1H), 7.88 (s, 1H), 7.74–7.61 (m, 4H), 6.37 (dq, J_{H-H} = 16.1 Hz, J_{H-F} = 6.5 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.1 (q, J_{C-F} = 6.7 Hz), 131.2, 131.1, 130.5, 130.3, 130.0, 129.2, 127.7, 127.2, 127.2, 127.2, 126.4, 124.3, 123.4, 123.4 (q, J_{C-F} = 269.7 Hz), 122.8, 119.5 (q, J_{C-F} = 33.6 Hz) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ -63.5 (d, J_{H-F} = 6.7 Hz, 3F) ppm. The ^{1}H NMR and ^{19}F NMR spectral data are in accordance with the literature report.[4d]

2t: *1,4-bis((E)-3,3,3-trifluoroprop-1-en-1-yl)benzene.* Prepared according to the general procedure and purified by flash column chromatography (hexane). White solid, 40 mg, 75%. R_f = 0.42 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (s, 4H), 7.15 (dq, J_{H-H} = 16.2 Hz, J_{H-F} = 2.1 Hz, 2H), 6.25 (dq, J_{H-H} = 16.2 Hz, J_{H-F} = 6.5 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.8 (q, J_{C-F} = 6.7 Hz), 135.1, 128.2, 123.5 (q, J_{C-F} = 268.9 Hz), 117.2 (q, J_{C-F} = 34.1 Hz) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ -63.5 (d, J_{H-F} = 6.7 Hz, 3F) ppm. The ^{1}H NMR and ^{19}F NMR spectral data are in accordance with the literature report.[27]

2u: *(E)-2-(3,3,3-trifluoroprop-1-en-1-yl)pyridine.* Prepared according to the general procedure and purified by flash column chromatography (25% Et_2O/hexane).

Pale-yellow oil, 52 mg, 30% (1 mmol scale). R_f = 0.60 (20% EtOAc/hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.64 (d, J_{H-H} = 4.2 Hz, 1H), 8.64 (td, J_{H-H} = 7.7, 1.7 Hz, 1H), 7.35 (d, J_{H-H} = 7.7 Hz, 1H), 7.28 (dd, J_{H-H} = 7.6, 5.3 Hz, 1H), 7.18 (dq, J_{H-H} = 15.7 Hz, J_{H-F} = 2.0 Hz, 1H), 6.81 (dq, J_{H-H} = 15.7 Hz, J_{H-F} = 6.9 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.9, 150.2, 137.0, 136.8 (q, J_{C-F} = 6.6 Hz), 124.4, 124.0, 123.6 (q, J_{C-F} = 268.8 Hz), 120.2 (q, J_{C-F} = 34.1 Hz) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ-63.9 (dd, J_{H-F} = 6.8, 2.2 Hz) ppm. The spectral data are in accordance with the literature report.[5g]

2v: *(E)-3-(3,3,3-trifluoroprop-1-en-1-yl)thiophene.* Prepared according to the general procedure and purified by flash column chromatography (pentane). Colorless oil, 70 mg, 40% (1 mmol scale). R_f = 0.72 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (d, J_{H-H} = 2.4 Hz, 1H), 7.35 (dd, J_{H-H}= 5.0, 3.0 Hz, 1H), 7.24 (dd, J_{H-H}= 5.1, 1.0 Hz, 1H), 7.15 (dq, J_{H-H} = 16.1 Hz, J_{H-F} = 2.1 Hz, 1H), 6.05 (dq, J_{H-H} = 16.1 Hz, J_{H-F} = 6.6 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.4, 131.5 (q, J_{C-F} = 7.0 Hz), 127.3, 127.1, 125.0, 123.8 (q, J_{C-F} = 268.7 Hz), 115.6 (q, J_{C-F} = 33.9 Hz) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ -63.3 (d, J_{H-F} = 7.0 Hz) ppm. The spectral data are in accordance with the literature report.[5e]

2w: *(E)-(((4,4,4-trifluorobut-2-en-1-yl)oxy)methyl)benzene.* Prepared according to the general procedure and purified by flash column chromatography (5% EtOAc/hexane),

containing 4% of inseparable side product **3w**. Colorless oil, 18 mg, 43%. R_f = 0.70 (10% EtOAc/hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39–7.30 (m, 5H), 6.44 (doublet of octuplets, J_{H-H} = 15.8 Hz, J_{H-F} = 2.0 Hz, 1H), 6.03–5.92 (m, 1H), 4.58 (s, 2H), 4.15–4.11 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.6, 136.6 (q, J_{C-F} = 6.4 Hz), 128.7, 128.1, 127.8, 123.2 (q, J_{C-F} = 269.2 Hz), 118.9 (q, J_{C-F} = 34.1 Hz), 73.1, 67.9 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ -64.3 (m, 3F) ppm. The spectral data are in accordance with the literature report.[28]

2x: *(E)-1,1,1-trifluorotridec-2-ene.* Prepared according to the general procedure and purified by flash column chromatography (hexane), obtained as an inseparable mixture with **3x** (**2x**:**3x** = 2.4:1). Colorless oil, 24 mg, 35%. R_f = 0.85 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.42–6.34 (m, 1H), 5.64–5.56 (m, 1H), 2.18–2.11 (m, 2H), 1.45–1.27 (m, 16H), 0.88 (t, J_{H-H} = 6.8 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.0 (q, J_{C-F} = 6.5 Hz), 123.3 (q, J_{C-F} = 268.8 Hz), 118.4 (q, J_{C-F} = 33.1 Hz), 32.1, 31.6, 29.7, 29.7, 29.5, 29.5, 29.2, 28.1, 22.8, 14.3 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ -63.9 (m, 3F) ppm. The spectral data are in accordance with the literature report.[8d]

6a: *(E)-(3,3,3-trifluoro-2-methylprop-1-en-1-yl)benzene.* Prepared according to the general procedure and purified by flash column chromatography (pentane), containing 5% of inseparable isomer *Z*-**6a**. Colorless oil, 61.5 mg (1 mmol scale), 33%. R_f = 0.68 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44–7.34 (m, 5H), 7.08 (s, 1H), 2.04 (s, 3H)

ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.7, 131.4 (q, $J_{C\text{-}F}$ = 6.2 Hz), 129.3, 128.6, 128.4, 126.4 (q, $J_{C\text{-}F}$ = 28.8 Hz), 124.7 (q, $J_{C\text{-}F}$ = 272.7 Hz), 12.3 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ -69.5 (s, 3F) ppm. The ^{1}H NMR and ^{19}F NMR spectral data are in accordance with the literature report.[5g]

7a: *2-(3,3,3-trifluoro-2-(trifluoromethyl)prop-1-en-1-yl)naphthalene.* Prepared according to the general procedure and purified by flash column chromatography (hexane). White solid, 49 mg, 85%. R_f = 0.70 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93–7.86 (m, 4H), 7.80 (s, 1H), 7.60–7.51 (m, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.4 (m), 134.0, 132.8, 130.4, 128.8, 128.5, 128.5, 128.0, 127.9, 127.1, 125.6 (q, $J_{C\text{-}F}$ = 2.6 Hz), 121.7 (qq, $J_{C\text{-}F}$ = 273.2, 2.2 Hz), 121.1 (q, $J_{C\text{-}F}$ = 274.8 Hz), 120.4 (quint, $J_{C\text{-}F}$ = 32.5 Hz) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ -57.5 (q, $J_{F\text{-}F}$ = 7.2 Hz, 3F), -63.5 (q, $J_{F\text{-}F}$ = 7.2 Hz, 3F) ppm. IR (KBr): 1657, 1363, 1295, 1219, 1129, 969 cm^{-1}. HRMS m/z (EI): calcd. for $C_{14}H_8F_6$ $[M]^+$: 290.0525; found: 290.0526.

7b: *1-methoxy-4-(3,3,3-trifluoro-2-(trifluoromethyl)prop-1-en-1-yl)benzene.* Prepared according to the general procedure and purified by flash column chromatography (5% EtOAc/hexane). Pale-yellow oil, 26 mg, 48%. R_f = 0.60 (10% EtOAc/hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (s, 1H), 7.45 (d, $J_{H\text{-}H}$ = 8.8 Hz, 2H), 6.94 (d, $J_{H\text{-}H}$ = 8.8 Hz, 2H), 3.86 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.9, 142.7 (m), 132.2 (q, $J_{C\text{-}F}$ = 2.8 Hz), 123.2, 122.0 (qq, $J_{C\text{-}F}$ = 272.7, 2.5 Hz), 121.4 (q, $J_{C\text{-}F}$ = 274.3 Hz), 117.3

(quint, $J_{C\text{-}F}$ = 32.3 Hz), 55.5 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ-57.5 (q, $J_{F\text{-}F}$ = 7.5 Hz, 3F), -63.5 (q, $J_{F\text{-}F}$ = 7.7 Hz, 3F) ppm. The ^{1}H NMR and ^{19}F NMR spectral data are in accordance with the literature report.[22b,d]

7c: *ethyl 4-(3,3,3-trifluoro-2-(trifluoromethyl)prop-1-en-1-yl)benzoate.* Prepared according to the general procedure and purified by flash column chromatography (5% EtOAc/hexane). Pale-yellow oil, 50 mg, 80%. R_f = 0.58 (10% EtOAc/hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (d, $J_{H\text{-}H}$ = 8.4 Hz, 2H), 7.69 (s, 1H), 7.46 (d, $J_{H\text{-}H}$ = 8.2 Hz, 2H), 4.40 (q, $J_{H\text{-}H}$ = 7.1 Hz, 2H), 1.41 (t, $J_{H\text{-}H}$ = 7.1 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.8, 142.3 (m), 135.4, 132.2, 129.8, 128.8, 122.5 (quint, $J_{C\text{-}F}$ = 32.4 Hz), 121.3 (qq, $J_{C\text{-}F}$ = 273.6, 2.2 Hz), 120.7 (q, $J_{C\text{-}F}$ = 275.3 Hz), 61.5, 14.4 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ-57.6 (q, $J_{F\text{-}F}$ = 7.1 Hz, 3F), -63.9 (q, $J_{F\text{-}F}$ = 7.1 Hz, 3F) ppm. IR (neat): 2986 (br), 1722, 1666, 1393, 1289 (br), 1170 (br), 977, 850 cm^{-1}. HRMS m/z (EI): calcd. for $C_{13}H_{10}F_6O_2$ $[M]^+$: 312.0580; found: 312.0580.

7d: *1-bromo-4-(3,3,3-trifluoro-2-(trifluoromethyl)prop-1-en-1-yl)benzene.* Prepared according to the general procedure and purified by flash column chromatography (pentane). Colorless oil, 48mg, 75%. R_f = 0.68 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (d, $J_{H\text{-}H}$ = 8.6 Hz, 2H), 7.56 (s, 1H), 7.29 (d, $J_{H\text{-}H}$ = 8.4 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.0 (m), 132.1, 130.8 (q, $J_{C\text{-}F}$ = 2.1 Hz), 129.9, 125.4, 121.5 (qq, $J_{C\text{-}F}$ = 273.4, 2.3 Hz), 121.3 (quint, $J_{C\text{-}F}$ = 32.3 Hz), 120.8 (q, $J_{C\text{-}F}$ = 275.2 Hz) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ -57.7 (q, $J_{F\text{-}F}$ = 7.2 Hz, 3F), -63.8 (q, $J_{F\text{-}F}$ = 7.2 Hz, 3F) ppm. IR (neat): 2930 (br), 1661, 1395, 1292, 1166 (br), 977, 830 cm^{-1}. HRMS m/z (EI): calcd. for $C_{10}H_5BrF_6$ $[M]^+$: 317.9473; found: 317.9473.

7e: *9-(3,3,3-trifluoro-2-(trifluoromethyl)prop-1-en-1-yl)phenanthrene.* Prepared according to the general procedure and purified by flash column chromatography (hexane). White solid, 47 mg, 70%. R_f = 0.40 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.75 (d, $J_{H\text{-}H}$= 8.3 Hz, 1H), 8.69 (d, $J_{H\text{-}H}$= 8.3 Hz, 1H), 8.19 (s, 1H), 7.92 (d, $J_{H\text{-}H}$= 7.5 Hz, 1H), 7.76–7.63 (m, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.7 (m), 131.0, 130.7, 130.3, 129.5, 129.2, 128.2, 127.8, 127.7, 127.5, 127.4, 127.4, 125.0, 123.8 (quint, $J_{C\text{-}F}$ = 32.0 Hz), 123.5, 122.8, 121.5 (q, $J_{C\text{-}F}$ = 273.7 Hz), 121.0 (q, $J_{C\text{-}F}$ = 275.5 Hz) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ -57.6 (q, $J_{F\text{-}F}$ = 7.0 Hz, 3F), -63.6 (q, $J_{F\text{-}F}$ = 6.9 Hz, 3F) ppm. IR (KBr): 1664, 1390, 1298, 1215, 1140, 975, 742 cm^{-1}. HRMS m/z (EI): calcd. for $C_{18}H_{10}F_6$ $[M]^+$: 340.0681; found: 340.0681.

Procedure for the one-pot synthesis of 2a from TMS-protected alkyne 1a' (Scheme 3): TMS-protected alkyne 1a' (0.2 mmol, 1.0 equiv.), B_2Pin_2 (0.24 mmol, 1.2 equiv.) and DMF (3 mL) were added to a 10 mL RBF with a magnetic stir bar. Then the flask was sealed with a septa and flushed with argon. TBAF (0.22 mmol, 1.1 equiv.) and fluoroform-derived $CuCF_3$ (0.4 M in DMF, 1.0 mL, 2.0 equiv.) were then added subsequently under argon. Then the septa was removed and the mixture was

stirred in air at room temperature for 8 h. The reaction was filtered through a short pad of silica gel and rinsed with 30% diethyl ether in hexanes (100 mL) and then concentrated by rotary evaporator. The crude mixture was purified by flash column chromatography on silica gel.

Procedure for the hydrotrifluoromethylation of alkyne 1a using Togni's reagent (Scheme 2, Condition A): alkyne **1a** (0.1 mmol, 1.0 equiv.), B_2Pin_2 (0.1 mmol, 1.0 equiv.), CuCl (0.2 mmol, 2.0 equiv.) and Togni's reagent (0.2 mmol, 2.0 equiv.) were added to a test tube with a magnetic stir bar. The flask was sealed with a septa and flushed with argon. DMF (1 mL) was added. Then the septa was removed and mixture was stirred in air at room temperature for 8 h.

Procedure for the hydrotrifluoromethylation of alkyne 1a using CuCl/TMSCF$_3$ system[13] (Scheme 2, Condition B): alkyne **1a** (0.1 mmol, 1.0 equiv.), B_2Pin_2 (0.1 mmol, 1.0 equiv.), CuCl (0.2 mmol, 2.0 equiv.) and KF (1 mmol, 10.0 equiv.) were added to a test tube with a magnetic stir bar. The flask was sealed with a septa and flushed with argon. DMF (1 mL) and $TMSCF_3$ (1 mmol, 10.0 equiv.) were added. Then the septa was removed and the mixture was stirred in air at room temperature for 8 h.

Procedure for the hydrotrifluoromethylation of alkyne 1a using (PPh$_3$)$_3$CuCF$_3$ complex[14] (Scheme 2, Condition C): alkyne **1a** (0.1 mmol, 1.0 equiv.), B_2Pin_2 (0.1

mmol, 1.0 equiv.) and $(PPh_3)_3CuCF_3$ complex (0.2 mmol, 2.0 equiv.) were added to a test tube with a magnetic stir bar. The flask was sealed with a septa and flushed with argon. DMF (1 mL) was added. Then the septa was removed and the mixture was stirred in air at room temperature for 8 h.

Procedure for the synthesis of (*Z*)-vinyl BPin 8a'[29]: Under argon, to a round-bottom flask equipped with a magnetic stir bar was added $[Rh(cod)_2Cl_2]$ (6.6 mg. 0.015 mmol, 0.015 equiv.) and Cy_3P (16.8 mg, 0.06 mmol, 0.06 equiv.), then 3 ml THF and Et_3N (0.69 mL, 5 mmol, 5.0 equiv.) was added sequentially. The mixture was stirred for 5 minutes to reach complete dissolution and formation of the catalytic complex *in situ*. Next, pinacolborane (154 mg, 1.2 mmol, 1.2 equiv.) was added to the solution of catalyst followed by the addition of the 2-ethynylnaphthalene (152 mg, 1 mmol, 1.0 equiv.). The mixture was stirred at room temperature for 4 hours. After completion, the solvent was evaporated and the crude product was directly purified by flash column chromatography on silica gel using hexanes/EtOAc = 30:1 to obtain the *E/Z* mixture of vinyl BPin (*E*/*Z* = 56:44) **8a** and **8a'** as a yellow oil (180 mg, 0.64 mmol, 64%). R_f= 0.60 (hexanes/EtOAc = 8:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (s, 0.8 H, **8a'**), 7.90 (s, 1H, **8a**), 8.19 (s, 1H), 7.87–7.78 (m, 7.2 H), 7.74 (d, $J_{H\text{-}H}$= 15.6 Hz, 0.8 H, **8a'**), 7.67 (d, $J_{H\text{-}H}$= 18.4 Hz, 1 H, **8a**), 7.51–7.42 (m, 3.6 H), 6.39 (d, $J_{H\text{-}H}$= 18.4 Hz, 1 H, **8a**), 5.77 (d, $J_{H\text{-}H}$= 15.0 Hz, 0.8 H, **8a'**), 1.39 (s, 12 H, **8a**), 1.36 (s, 9.2H, **8a'**) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ 149.6 (**8a**), 148.2 (**8a'**), 136.1 (**8a'**), 135.0 (**8a**), 133.8 (**8a**), 133.5 (**8a**), 133.3 (**8a'**), 133.2 (**8a'**), 128.4 (**8a**), 128.3 (**8a**), 128.2 (**8a'**), 128.1 (**8a'**), 128.1 (**8a**), 127.7 (**8a**), 127.6 (**8a'**), 127.5 (**8a'**), 126.6 (**8a'**), 126.5 (**8a**), 126.3 (**8a**), 126.1 (**8a'**), 126.0 (**8a'**), 123.4 (**8a**), 83.6 (**8a'**), 83.4 (**8a**), 24.9 ppm. IR (neat): 3051, 2980, 1619, 1329 (br), 1263, 1147, 923, 823 cm^{-1}. HRMS m/z (ESI): calcd. for $C_{18}H_{21}BO_2Na$ $[M+Na]^+$: 303.1527; found: 303.1525.

Procedure for the trifluoromethylation of vinyl BPin[16b] (Scheme 5b): vinyl BPin **8a** or the mixture of **8a** and **8a'** (0.2 mmol, 1.0 equiv.) and DMF (3 mL) were added to a 10 mL RBF with a magnetic stir bar. The fluoroform-derived $CuCF_3$ (0.4 M in DMF, 1.0 mL, 2.0 equiv.) was then added. The mixture was stirred in air at room temperature for 5 h. The reaction was filtered through a short pad of silica gel and rinsed with 30% diethyl ether in hexanes (100 mL) and then concentrated by rotary evaporator. The crude mixture was purified by flash column chromatography on silica gel to obtain **2a** or mixture of *E/Z* product **2a** and **2a'** (*E/Z* = 57:43).

(Z)-2-(3,3,3-trifluoroprop-1-en-1-yl)naphthalene (**2a'**): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90–7.85 (m, 4H), 7.60–7.53 (m, 3H), 7.09 (d, $J_{H\text{-}H}$ = 12.6 Hz, 1H), 5.87 (dq, $J_{H\text{-}H}$ = 12.6 Hz, $J_{H\text{-}F}$ = 9.1 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.8 (q, $J_{C\text{-}F}$ = 6.0 Hz), 133.4, 133.1, 131.2, 128.6, 128.1, 127.8, 127.1, 126.6, 126.1 (q, $J_{C\text{-}F}$ = 2.7 Hz), 123.1 (q, $J_{C\text{-}F}$ = 271.2 Hz), 118.2 (q, $J_{C\text{-}F}$ = 34.9 Hz) ppm. ^{19}F NMR (376 MHz, $CDCl_3$):

δ -57.4 (d, $J_{H\text{-}F}$ = 9.1 Hz, 3F) ppm. The spectral data are in accordance with the literature report.[30]

ASSOCIATED CONTENT

Supporting Information

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

Detailed optimization studies and spectral data (^{1}H, ^{13}C, ^{19}F NMR) (PDF)

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Notes

The authors declare no competing financial interest.

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