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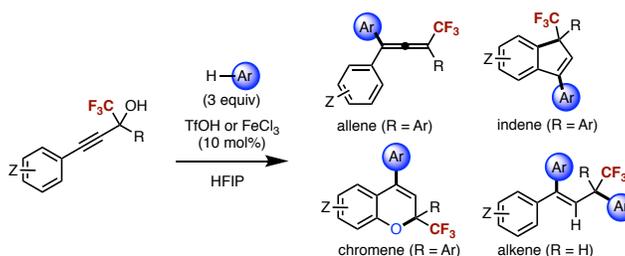
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Catalytic Synthesis of Trifluoromethylated Allenes, Indenes, Chromenes and Olefins from Propargylic Alcohols in HFIP

Florent Noël, Vuk D. Vuković, Jing Yi, Edward Richmond, Pavle Kravljjanac and Joseph Moran*

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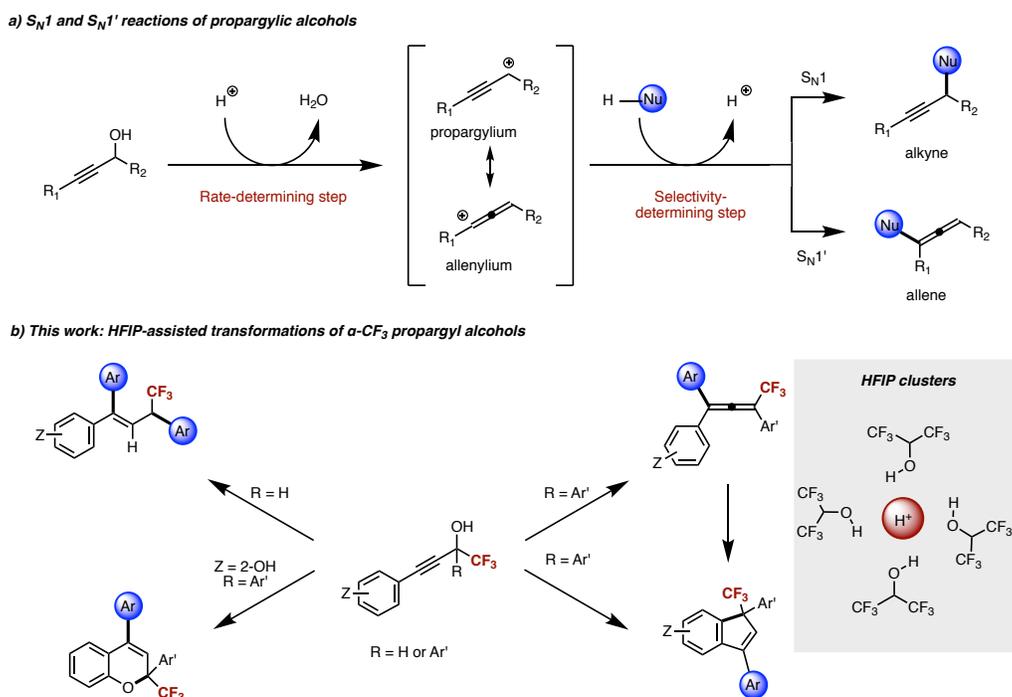
Abstract

A general method to access CF₃-substituted allenes from propargylic alcohols under Lewis acid catalysis in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) as solvent is described. By tuning the reaction time and temperature, the obtained allenes rearrange to 1,3-biaryl-1-trifluoromethyl-1*H*-indenes. By tuning the structure of the propargylic alcohol substrates, a range of trifluoromethylated 2*H*-chromenes were successfully synthesized, with use of catalytic quantities of strong Brønsted acid in HFIP. The present method is therefore highly potent for synthesis of a number of potentially pharmaceutically interesting new trifluoromethylated compounds and produces water as the only stoichiometric byproduct.

INTRODUCTION

Propargylic alcohols represent an attractive class of starting compounds for a number of chemical transformations.¹ The direct nucleophilic substitution of propargylic alcohols can result in two types of products: an α -substituted alkyne or an allene (Scheme 1a).² The transformations leading to alkynes are well studied.³ On the other hand, there are few examples of the formation of allenes from propargyl alcohols through carbocationic intermediates.⁴ Generally, carbocationic

intermediates bearing an adjacent electron-withdrawing group, such as a CF₃ group, are difficult to form. They are typically generated from halides or pseudo-halides.⁵ In some cases, they have been generated from alcohols in the presence of superstoichiometric quantities of Brønsted or Lewis acids.^{6,7} Catalytic methods for their generation are desirable because substituting hydrogen atoms for fluorine atoms is well known to modulate a molecule's physico-chemical and pharmaceutically relevant properties,⁸ such as its pharmacokinetics and binding affinity.⁹ One of the most suitable organic solvents used to carry out reactions involving short-lived carbocations is 1,1,1,3,3,3-hexafluoroisopropanol (HFIP).¹⁰ We recently reported that Brønsted acid catalyzed Friedel-Crafts reactions of α -trifluoromethylated benzylic alcohols proceed with ease *via* α -trifluoromethyl carbocationic species in HFIP.¹¹ As a continuation of this research program, we explored the reactivity of α -trifluoromethylated propargylic alcohols in HFIP under Brønsted and Lewis acid catalysis. Here we show that CF₃-bearing propargyl alcohols are versatile substrates in dehydroarylativ Friedel-Crafts reactions (Scheme 1b), giving access to a number of trifluoromethylated allenes, indenenes, chromenes and alkenes. The method is of use for the diversity-oriented synthesis of trifluoromethylated compounds, which are of considerable interest to pharmaceutical research,¹² and produces water as the only stoichiometric byproduct.

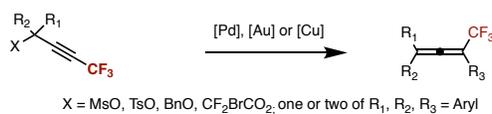


Scheme 1. HFIP-assisted transformation of α -CF₃ propargyl alcohols.

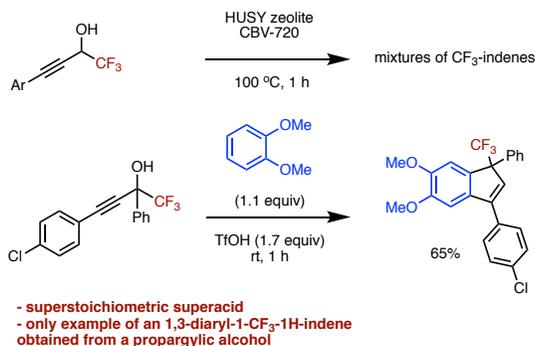
Methods for the synthesis of allenes bearing electron-withdrawing groups, such as keto, carboxy, ester, amide, cyano, sulfone groups have been described.¹³ Among them, only a limited number allow access to monoaryl¹⁴ and biaryl¹⁵ mono(CF₃) substituted allenes (Scheme 2a). A single example of the Pd-catalyzed synthesis of triaryl mono(CF₃) substituted allenes is known.¹⁶ To our knowledge, no *general catalytic* methods allowing access to triaryl mono(CF₃) substituted allenes have been reported so far. Furthermore, methods for CF₃-allene synthesis proceeding *via* carbocationic intermediates have not been described.

Methods for the synthesis of indenenes bearing CF₃-groups at the C1-C3 positions are known but are limited in terms of the substitution patterns that can be achieved. Reported strategies include the treatment of indanones with perfluoroalkyl lithium reagents¹⁷ and the use of α -(trifluoromethyl)allyl alcohols.^{18,19} In general, indenenes can be prepared by the isomerization of allenes,²⁰ but the preparation of CF₃-indenenes through the intermediacy of CF₃-allenes, reported herein, had not been described. However, during the preparation of this manuscript, Vasilyev, Nenajdenko, Krasavin and collaborators reported a single example of the conversion of a propargylic alcohol to a CF₃-indene using neat sulfuric or triflic acid as solvent,²¹ or zeolites²² under high pressure and temperature conditions (Scheme 2b). Herein we report the first general method for the synthesis of 1,3-biaryl-1-trifluoromethyl-1*H*-indenenes, which employs a Brønsted acid catalyzed approach under significantly milder conditions. Moreover, by tuning of the reaction time and temperature, the corresponding intermediate triaryl CF₃ allenes can be accessed.

a) Previous work on CF₃-allene synthesis from propargyl alcohol derivatives with activated leaving group



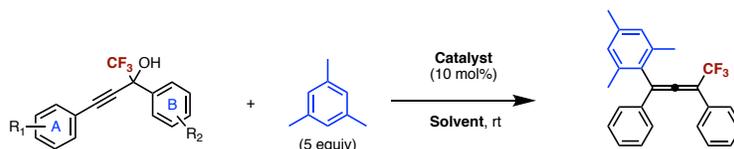
b) Recent work on CF₃-indene synthesis from propargylic alcohols



Scheme 2. Previous reports on CF₃-allene and -indene synthesis

RESULTS AND DISCUSSION

Reaction discovery and optimization. We began our investigations with standard conditions for dehydroarylation reactions of benzylic alcohols in HFIP that were previously established.¹¹ Instead of direct nucleophilic substitution on the α -CF₃ carbon of alcohol **1**, with TfOH as catalyst in HFIP at room temperature we observed the nucleophile attack on γ -carbon and formation of allene **1a** (Table 1, entry 1). When the same reaction is conducted at higher temperature (50 °C), the formation of an additional product (CF₃-substituted indene, **2a**) was observed (entry 2). Weaker Brønsted acids did not lead to the formation of allene or indene (entries 3-5). The stronger fluoroantimonic acid gave a mixture of allene and indene in an approximate ratio of 11:1 (entry 6). Some Lewis acid catalysts provided the allene, but not the corresponding indene in significant yield (entries 7-11). However, FeCl₃ led to the formation of the allene in 93% isolated yield in 10 min (entry 12). Heating at 80 °C after longer reaction times led to complete transformation to the corresponding indene (entry 13). By testing the same reaction in other solvents (entries 14-16), we confirmed that this reactivity is optimal in HFIP. Iron(II) chloride was not as efficient as iron(III) chloride (entry 17).

Table 1. Reaction optimization and discovery

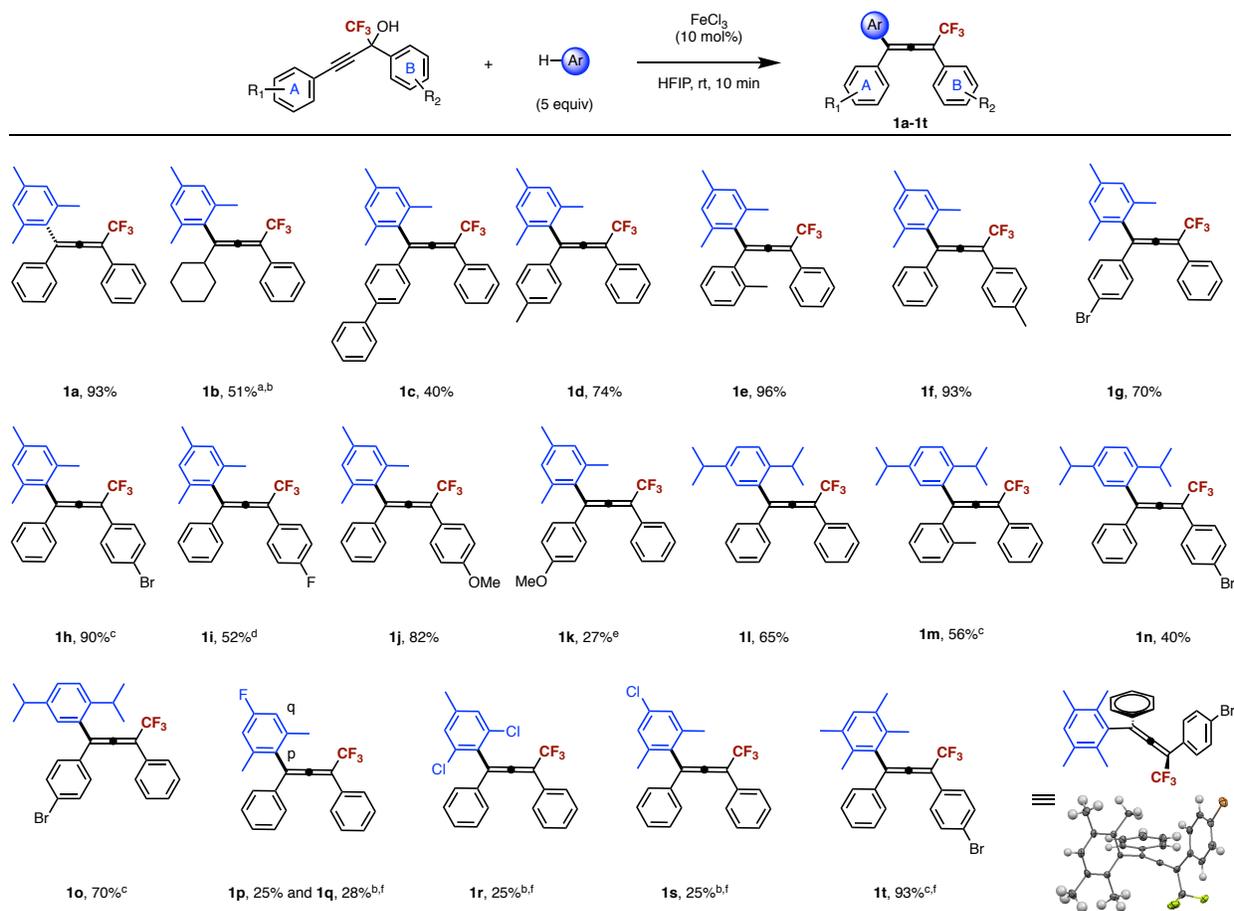
entry	catalyst	solvent	time	yield 1a (%)	yield 2a (%)
1	TfOH	HFIP	1 h	85	-
2 ^a	TfOH	HFIP	45 min	50	43
3 ^a	TFA	HFIP	24 h	60	-
4	H ₃ PO ₄	HFIP	24 h	-	-
5	HCl ^b	HFIP	10 min	traces	-
6	HSbF ₆ ·6H ₂ O	HFIP	10 min	87	8
7	Sc(OTf) ₃	HFIP	24 h	9	-
8	SbF ₅	HFIP	10 min	66	-
9 ^a	AlCl ₃	HFIP	45 min	24	10
10	ZnCl ₂	HFIP	24 h	7	-
11	AuCl ₃	HFIP	10 min	69	-
12	FeCl ₃	HFIP	10 min	93	-
13 ^c	FeCl ₃	HFIP	24 h	-	94
14	FeCl ₃	<i>i</i> -PrOH	10 min	-	-
15	FeCl ₃	CF ₃ CH ₂ OH	10 min	39	-
16	FeCl ₃	CH ₂ Cl ₂	24 h	9	-
17	FeCl ₂	HFIP	24 h	41	-

^aPerformed at 50 °C. ^b37% aq. HCl (w/w) was used. ^cPerformed at 80 °C.

Scope of trifluoromethylated allenes. Encouraged by the initial results, the scope of triaryl monotrifluoromethyl allenes was explored (Table 2). The parent 1,1,1-trifluoro-2,4-diphenyl-but-3-yn-1-ol (**1**) furnished the corresponding allene **1a** with mesitylene as nucleophile in 93% yield. Replacement of the phenyl ring A with cyclohexyl (**1b**) or biphenyl (**1c**) groups lead to a significant decrease in yield, but with *p*-tolyl substitution this decrease was less pronounced (**1d**). However, *o*-methyl substitution of ring A (**1e**) or *p*-methyl substitution of ring B (**1f**) did not influence the yield significantly. *p*-Bromo substitution of phenyl rings A or B slowed down the reaction (**1g** and **1h**), which could be overcome in most cases by increasing the reaction time (**1h**). As expected, an electron-withdrawing (*p*-fluoro) substituent on phenyl ring B had a deactivating influence (**1i**). However, electron-donating (*p*-methoxy) groups also led to lower yields, due to rapid subsequent

indene-forming reactions (**1j**). The same is true when an electron-donating *p*-methoxy group is present on ring A. For example, attempts to isolate allene **1k** could only be accomplished in 27% yield by interrupting the reaction after 5 minutes. In these cases, attempts to isolate the allene by running at the reaction at lower temperatures or under different concentrations were unsuccessful since the subsequent cyclization is more facile than the initial allene formation. Finally, the use of bulkier nucleophiles such as 1,4-diisopropylbenzene also lead to decreased yields (**1l-1o**) as did less activated (Cl- and F- substituted) nucleophiles (**1p-1r**). To confirm the structure of the allenes, we obtained an X-ray crystal structure of allene **1s**.

Table 2. Scope of tetrasubstituted allenes bearing a CF₃ group

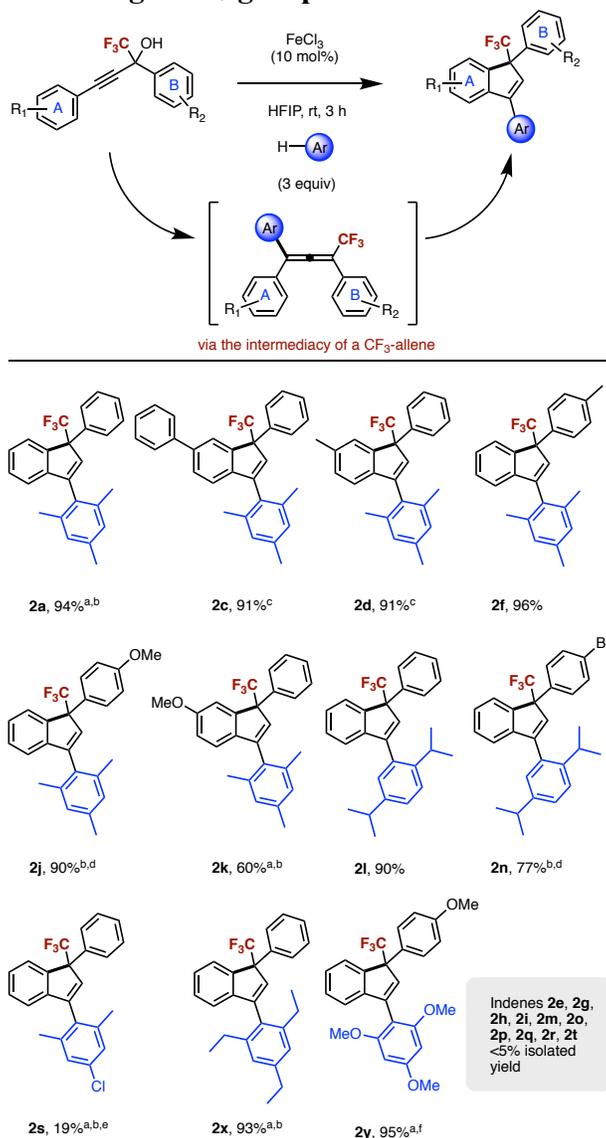


^aHeated at 50 °C. ^bReaction time was 24 h. ^cReaction time was 3 h. ^dReaction time was 1 h.

^eReaction time was 5 min. ^fHeated at 80 °C.

Scope of trifluoromethylated indenenes. In the next step of the study, the scope of indenenes was explored (Table 3). The indenenes **2a** and **2l** were obtained *via* allenes **1a** and **1l** in excellent yields. The indenenes **2c**, **2d** and **2f** substituted with phenyl or methyl groups were all obtained in excellent yields. When a methoxy group is attached in the *para* position on the phenyl ring B, the yield of the indene **2j** remained high, unlike the case of the *para* substituted phenyl ring A (**2k**). The reaction was slow down when a bromo-substituent was introduced in the phenyl ring B (**2n**). 1,3,5-Triethylbenzene proved to be a good nucleophile for formation of indenenes (entry **2x**). By increasing the temperature to 120 °C, it was possible to use 1,3,5-trimethoxybenzene as a nucleophile (entry **2y**). However, when a chloro-bearing arene was used, the yield dropped significantly (**2s**). In the case of indene **2x** and **2y**, we were unable to isolate the intermediate allene. Generally, attempts to form indenenes from propargylic alcohols using weaker arene nucleophiles *via* allenes were unsuccessful (for example, *via* allenes **1p-1q**), due both to the reduced ability of the nucleophile to capture the propargylic carbocation, as well as the subsequent deactivating effect of the electron-poor arene on the cyclization of the allene intermediate. Even under more forcing conditions, propargylic alcohols bearing a bromide or fluoride on ring A or ring B did not lead to indenenes, but instead stopped at the allenes (**1g**, **1h**, **1i**, **1o**, **1s**) previously described in Table 2.

Table 3. Scope of indenenes bearing a CF₃ group

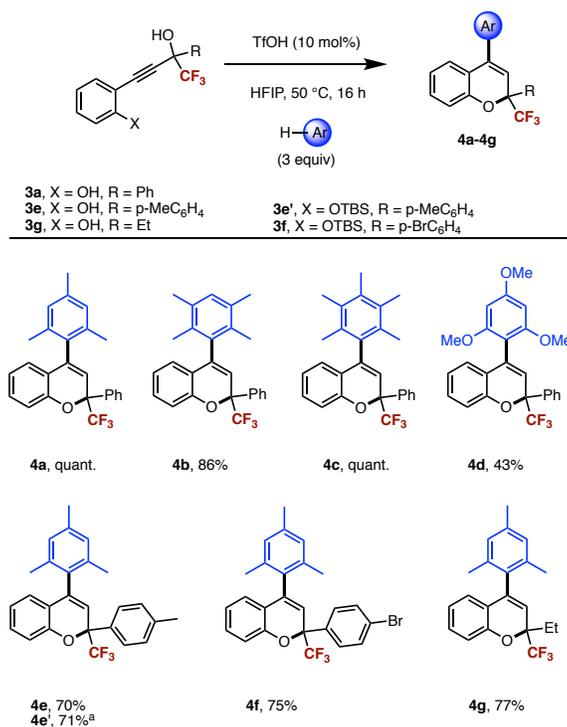


^aReaction time was 24 h. ^bHeated at 80 °C. ^cCarried out at 50 °C for 6 h. ^dReaction time was 1 h. ^eIsolated as mixture of regioisomers. ^fHeated at 120 °C.

Access to 2*H*-2-trifluoromethyl chromenes. We hypothesized that propargylic alcohols with an *o*-hydroxyphenyl moiety should give access to corresponding 2*H*-2-trifluoromethyl chromenes. Chromenes (benzopyrans) are a class of organic compounds that exhibit various biological activities,²³ especially their trifluoromethylated derivatives.²⁴ Here, we found that the catalytic use of TfOH gave higher yields than FeCl₃. Indeed, when 1,1,1-trifluoro-4-(2-hydroxyphenyl)-2-phenylbut-3-yn-1-ol (**3a**) was subjected to 10 mol% TfOH/in HFIP,²⁵ we were pleased to observe formation of chromene **4a** in quantitative yield (Table 4). Other nucleophiles such as durene,

pentamethylbenzene and 1,3,5-trimethoxybenzene proved to be compatible with the reaction conditions (**4b-4d**). Slight modifications to the electronic properties of the 2-phenyl ring (**4e** and **4f**) or replacement of the 2-aryl moiety with a 2-alkyl group (**4g**) were tolerated. Furthermore, the *tert*-butyl-dimethylsilyl ether derivatives **3e'** and **3f** yielded the same product as their phenolic precursors (**3e**), due to an *in situ* deprotection/cyclization on 1 mmol scale.

Table 4. Scope of chromenes bearing trifluoromethyl group

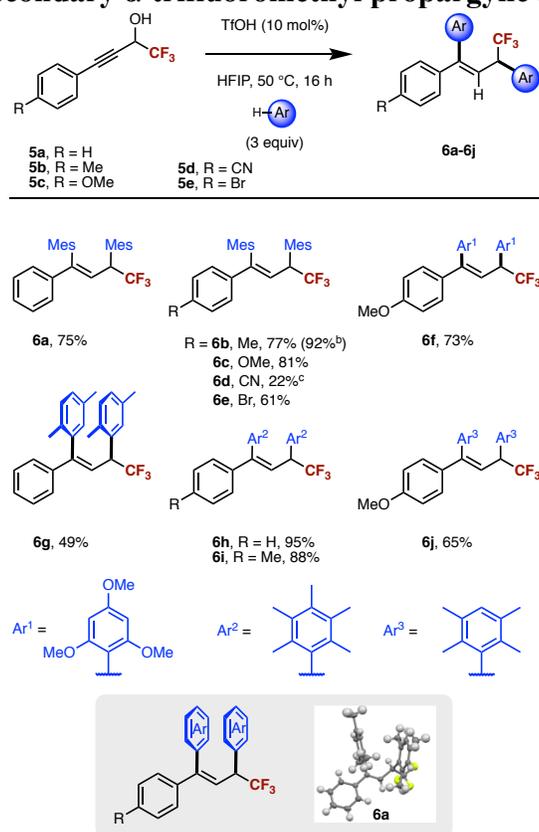


^aPerformed on 1 mmol scale.

Reactivity of secondary α -trifluoromethyl propargylic alcohols in HFIP. In light of the successful reactions of tertiary CF₃-propargylic alcohols, we next tested the reactivity of secondary CF₃-propargylic alcohols in the presence of catalytic TfOH. Unexpectedly, by applying the same reaction conditions, a bis-arylated alkene **6a** was observed (Table 5). An X-ray crystal structure of the product **6a** revealed the *Z*-geometry of the double bond, as well as a preferred conformation in which the two mesityl units are aligned. A series of *para*-substituted secondary α -trifluoromethyl propargylic alcohols was tested for Friedel-Crafts reactions with methyl- and methoxy-substituted benzenes as nucleophiles (Table 5). Methyl- (**5b**) and methoxy-

(**5c**) substituted propargyl alcohols furnished products **6b** and **6c** in slightly higher yields than the parent alcohol **6a**. Substitution with a cyano-group led to significant loss in reactivity (**6d**). In addition to the electronic deactivating effect of the CN group, the lowered yield may also potentially be due to the ability of this mildly basic group to buffer the Brønsted acid catalyst. The less electron-withdrawing bromine substituent led only to a minor drop in yield (**6e**). When 1,3,5-trimethoxybenzene was used as nucleophile, substantially lower yield of **6f** was obtained with the parent alcohol **5a**. However, methoxy-substituted alcohol **5c** furnished the corresponding product **6g** in good yield. With other methyl-substituted benzenes, such as *p*-xylene (**6h**), pentamethylbenzene (**6i-j**) and durene (**6k**), as nucleophiles, reaction products were also obtained in good to excellent yields.

Table 5. Bis-addition to secondary α -trifluoromethyl propargylic alcohols^a

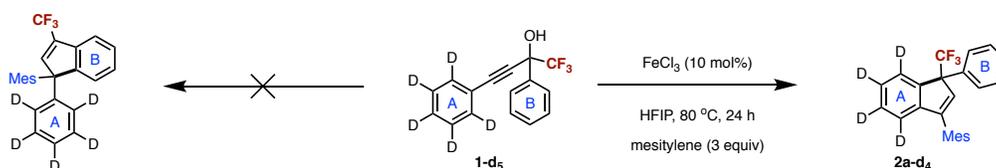


^aIsolated yields after column chromatography. ^bPerformed at 1 mmol scale.

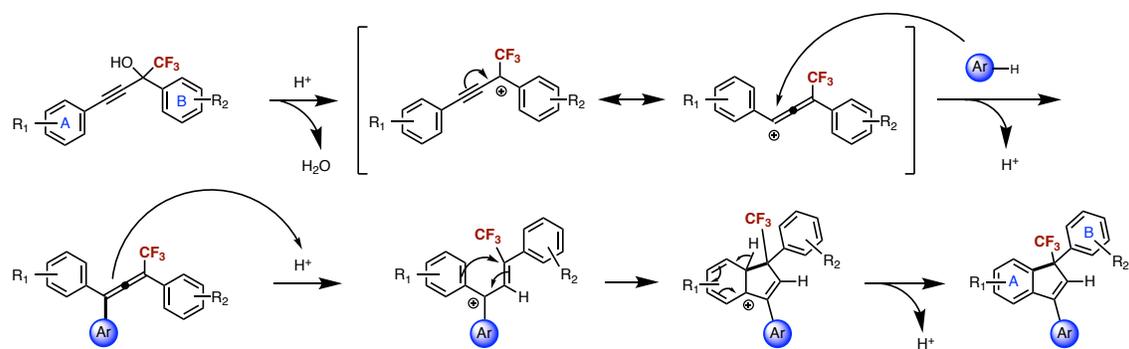
^cReaction heated at 100 °C for 88 h. Mes = mesityl.

Mechanistic experiments. To determine whether the FeCl_3 acts as a Lewis acid or Brønsted acid catalyst,⁷ reactions were carried out in the presence of catalytic quantities (10 mol%) of the hindered Brønsted base 2,6-di-*tert*-butylpyridine, which does not coordinate most metal ions,²⁶ and in the presence of a similar amount of Proton-sponge (1,8-Bis(dimethylamino)naphthalene, *N,N,N',N'*-Tetramethyl-1,8-naphthalenediamine). In both cases, no reaction was observed, suggesting that the role of the FeCl_3 is to generate a hidden Brønsted acid catalyst. However, substituting FeCl_3 with 10 mol% HCl gave only traces of product, excluding HCl as the active catalyst. Therefore, we suspect that the active catalytic species is a partially hydrated or HFIP-bound ferric ion that acts as a Brønsted acid catalyst, although rapid and complex equilibria between many possible species make this very difficult to determine definitively.

Insight into the mechanism of the cyclization of allenes to indenes can be extracted from the observed scope of substrates (Table 3). When a methyl group is in the *ortho* position on the phenyl ring A, like in the cases of **1e** and **1m**, the formation of the indene is disabled. *Para*-bromo substitution in phenyl ring A of the starting alcohols also leads to significantly lower cyclization rates of **1g** and **1o**. To distinguish whether ring A or ring B are involved in the indene-forming cyclization event, deuterated substrate **1-d₅** was exposed to the standard reaction conditions. Analysis of the ^1H and ^2H NMR and high resolution MS of the resulting product revealed its structure to be that of **2a-d₄** as shown in Scheme 3, consistent with a Nazarov-type cyclization involving ring A rather than one involving ring B (Scheme 4). Similar cyclizations have been reported to be catalyzed by $\text{Yb}(\text{OTf})_3$,²⁷ AgOTf , and TfOH .²⁸

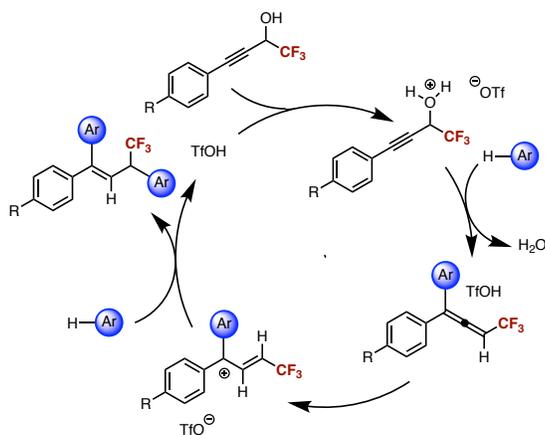


Scheme 3. Reaction of pentadeuterated substrate 1-d₅ with mesitylene



Scheme 4. Proposed mechanism of indene formation

Regarding the bis-addition of arenes to secondary propargylic alcohols (Table 5), the proposed mechanism is shown in Scheme 5. First, the hydroxyl group is activated by the TfOH/HFIP hydrogen-bond network, which is followed by nucleophilic substitution at the γ -carbon. Then, the C-C double bond that is more distant from the CF_3 group is protonated, forming a carbocation that is both benzylic and allylic. This carbocation is attacked by a second arene molecule, furnishing a tri-substituted allylic trifluoromethane.



Scheme 5. Plausible mechanism for bis-addition to secondary α - CF_3 propargylic alcohols

CONCLUSION

We have described a straightforward catalytic method to access triaryl CF_3 - bearing allenes, indenenes, chromenes and 1,1,1-trifluoro-3-butenes directly from α - CF_3 propargylic alcohols. The important role of HFIP solvent in combination with strong Brønsted or Lewis acids such as triflic acid or FeCl_3 were key to the observed reactivity. Mechanistic experiments suggest the initial

formation of a CF₃-allene intermediate, which subsequently cyclizes to the corresponding CF₃-indene.

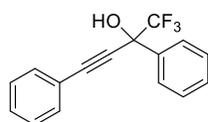
EXPERIMENTAL SECTION

General Information. All Friedel-Crafts reactions were performed in 10 mL glass pressure tubes under an atmosphere of air. Elevated temperatures were achieved by way of a stirrer-hotplate, metal heating block and thermocouple. Purification of reaction products was carried out by flash column chromatography using Merck silica gel (40-63 μ m). Analytical thin layer chromatography (TLC) was performed on aluminum sheets precoated with silica gel 60 F254 (Merck), cut to size. Visualization was accomplished with UV light. ¹H NMR spectra were recorded on a Bruker UltraShield Plus 400 (400 MHz) spectrometer at ambient temperature and are reported in ppm using solvent as internal standard (residual CHCl₃ at 7.26 ppm). ¹³C{¹H} NMR spectra were recorded on a Bruker UltraShield Plus 400 (100 MHz) spectrometer at ambient temperature and are reported in ppm using solvent as internal standard (CDCl₃ at 77.16 ppm). ¹⁹F NMR spectra were recorded on a Bruker UltraShield Plus 400 (376.5 MHz) spectrometer at ambient temperature and are reported in ppm using trifluoroacetic acid as external standard (peak at -76.55 ppm). Data are reported as: multiplicity (ap = apparent, br = broad, s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, m = multiplet, dd = doublet of doublets, ddd = doublet of doublet of doublets, dddd = doublet of doublet of doublet of doublets, qd = quartet of doublets, dt = doublet of triplets, dm = doublet of multiplets, td = triplet of doublets, quintd = quintet of doublets), coupling constants (in Hz) and integration. In cases where compounds were isolated as mixtures of regioisomers, signals corresponding to protons of the major regioisomer were integrated as integer values matching the number of protons in the molecule. Non-integer integration values correspond to signals of protons of minor regioisomers or to overlapping signals of regioisomers. GC/MS analysis was conducted on a GC System 7820A (G4320) connected to a MSD block 5977E (G7036A) using Agilent High Resolution Gas Chromatography Column HP-5MS UI, 30 m \times 0.250 mm \times 0.25 μ m. High resolution mass spectrometry (HRMS) analysis was performed on instruments GCT 1er Waters (EI and CI), MicroTOF-Q Bruker (ESI), and a GC Thermo Scientific Trace 1300 GC unit coupled to an APPI MasCom source mounted on a Thermo Scientific Exactive Plus EMR mass unit (Orbitrap FT-HRMS analyzer). **Materials:** All

commercial materials were purchased from Sigma-Aldrich, Alfa Aesar and FluoroChem, and were used as received, without further purification.

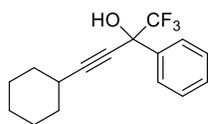
Preparation of tertiary propargylic alcohols

General procedure A for tertiary propargylic alcohols synthesis: Trifluoromethyl phenyl ketone (5.0-10 mmol, 1.0 equiv) and phenyl acetylene (1.5 equiv) were diluted in 10-15 mL DMSO. CuI (0.10 equiv) and K₂CO₃ (0.20 equiv) were added and the reaction mixture was heated at 50-70 °C for 24 h. The reaction mixture was then treated with brine, extracted with CH₂Cl₂, dried with anhydrous sodium sulfate and concentrated at reduced pressure. The product was then purified by silica gel column chromatography.

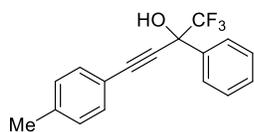


1,1,1-Trifluoro-2,4-diphenylbut-3-yn-2-ol was prepared according to general procedure A and isolated as a yellow oil. Spectral data are in agreement with the literature.²⁹ Isolated 2.55 g, 85% yield. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.86–7.79 (m, 2H), 7.57–7.52 (m, 2H), 7.48–7.42 (m, 3H), 7.42–7.32 (m, 3H),

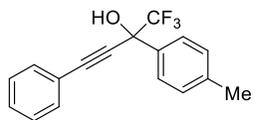
3.10 (s, 1H).



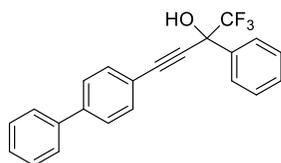
4-Cyclohexyl-1,1,1-trifluoro-2-phenylbut-3-yn-2-ol was prepared according to general procedure A and isolated as a yellow oil. Spectral data are in agreement with the literature.³⁰ Isolated 1.32 g, 44% yield. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.82-7.68 (m, 2H), 7.43-7.39 (m, 3H), 2.92 (s, 1H), 2.54 (sept. *J* = 4 Hz, 1H), 1.90-1.29 (m, 10H).



1,1,1-Trifluoro-2-phenyl-4-(p-toluy)but-3-yn-2-ol was prepared according to general procedure A and isolated as a pale yellow oil. Spectral data are in agreement with the literature.³¹ Isolated 2.55 g, 85% yield. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.86-7.78 (m, 2H), 7.52–7.36 (m, 5H), 7.17 (d, *J* = 7.8 Hz, 2H), 3.08 (s, 1H), 2.38 (s, 3H).

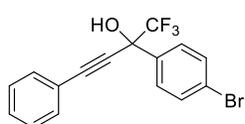


1,1,1-Trifluoro-4-phenyl-2-(p-toluy)but-3-yn-2-ol was prepared according to general procedure A and isolated as a yellow oil. Spectral data are in agreement with the literature.³² Isolated 0.93 g, 31% yield. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.62 (d, *J* = 8.1 Hz, 2H), 7.48–7.43 (m, 2H), 7.35–7.25 (m, 3H), 7.16 (d, *J* = 8.7 Hz, 2H), 2.98 (s, 1H), 2.31 (s, 3H).

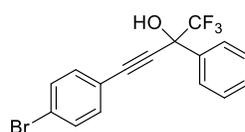


4-((1,1'-Biphenyl)-4-yl)-1,1,1-trifluoro-2-phenylbut-3-yn-2-ol was prepared according to general procedure A and isolated as yellow solid. Isolated 2.01 g, 67% yield. ¹H NMR (500 MHz, CDCl₃): δ (ppm) 7.86-7.80 (m, 2H), 7.63-7.57 (m, 6H), 7.48-7.42 (m, 4H), 7.38 (t, *J* = 7.4 Hz, 2H), 3.09 (s, 1H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ (ppm) 142.5,

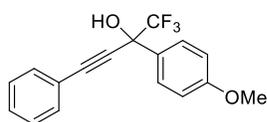
140.2, 135.4, 132.7, 129.7, 129.1, 128.4, 128.1, 127.4, 127.3, 127.2, 123.5 (q, $J = 283.9$ Hz), 119.9, 88.1, 85.1, 73.5 (q, $J = 32.3$ Hz), ^{19}F NMR (376.5 MHz, CDCl_3 , CF_3COOH - ext. st.): δ (ppm) – 80.9 (s, 3F). HRMS (APPI⁺-Orbitrap) m/z : $[\text{M}+\text{H}-\text{H}_2\text{O}]^+$: Calcd for $\text{C}_{22}\text{H}_{15}\text{F}_3\text{O}$ 335.1042; Found 335.1054 (3.5 ppm).



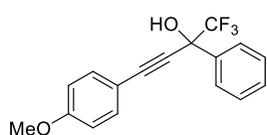
4-(4-Bromophenyl)-1,1,1-trifluoro-2-phenylbut-3-yn-2-ol was prepared according to general procedure A and isolated as a yellow oil. Spectral data are in agreement with the literature.¹³ Isolated 2.70 g, 90% yield. $R_f = 0.43$ (petroleum ether/EtOAc 9:1). ^1H NMR (500 MHz, CDCl_3): δ (ppm) 7.68 (d, $J = 8.6$ Hz, 2H), 7.58-7.50 (m, 4H), 7.44-7.35 (m, 3H), 3.26 (s, 1H).



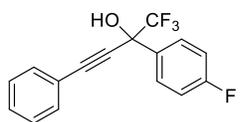
4-(4-Bromophenyl)-1,1,1-trifluoro-2-phenylbut-3-yn-2-ol was prepared according to general procedure A and isolated as a yellow oil. Spectral data are in agreement with the literature.¹³ Isolated 1.56 g, 52% yield. $R_f = 0.44$ (petroleum ether/EtOAc 9:1). ^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.75-7.69 (m, 2H), 7.46-7.41 (m, 2H), 7.39-7.34 (m, 3H), 7.34-7.28 (m, 2H), 3.09 (s, 1H).



1,1,1-Trifluoro-2-(4-methoxyphenyl)-4-phenylbut-3-yn-2-ol was prepared according to general procedure A and isolated as pale yellow solid. Spectral data are in agreement with the literature.³⁰ Isolated 1.92 g, 64% yield. ^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.73 (d, $J = 8.8$ Hz, 2H), 7.57-7.50 (m, 2H), 7.43-7.32 (m, 3H), 6.96 (d, $J = 8.9$ Hz, 2H), 3.84 (s, 3H), 3.10 (s, 1H).



1,1,1-Trifluoro-2-(4-methoxyphenyl)-4-phenylbut-3-yn-2-ol was prepared according to general procedure A and isolated as a yellow oil. Spectral data are in agreement with the literature.³⁰ Isolated 2.73 g, 91% yield. $R_f = 0.36$ (petroleum ether/EtOAc 9:1). ^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.73 (dt, $J = 8.8$ Hz, 3.0 Hz, 2H), 7.56-7.51 (m, 2H), 7.45-7.33 (m, 3H), 6.93-6.10 (m, 2H), 3.84 (s, 3H), 3.10 (s, 1H).



1,1,1-Trifluoro-2-(4-fluorophenyl)-4-phenylbut-3-yn-2-ol was prepared according to general procedure A and isolated as a yellow oil. Spectral data are in agreement with the literature.¹³ Isolated 2.85 g, 95% yield. $R_f = 0.40$ (petroleum ether/EtOAc 9:1). ^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.83-7.76 (m, 2H), 7.56-7.50 (m, 2H), 7.45-7.34 (m, 3H), 7.16-7.08 (m, 2H), 3.29 (s, 1H).

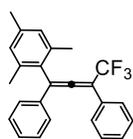
Preparation of allenens

General procedure B: To a 10 mL reaction tube was added the catalyst (10 mol%), HFIP (0.50 M relative to propargylic alcohol), propargylic alcohol (0.17-0.40 mmol, 1.0 equiv), followed by the arene nucleophile (5.0 equiv). The mixture was allowed to stir at 25 °C until judged complete by TLC (9:1 Petroleum ether:EtOAc), typically after 10 min. The reactions typically turn

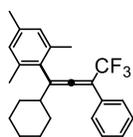
an opaque black. The crude reaction mixture was directly transferred for silica gel chromatography.

General procedure C: To a 10 mL reaction tube was added the catalyst (10 mol%), HFIP (0.5-1.0 M relative to propargylic alcohol), and propargylic alcohol (0.17-0.40 mmol, 1.0 equiv), followed by the arene nucleophile (5.0 equiv). The reactions typically turn an opaque black. After completion of the reaction as judged by TLC, the crude reaction mixture was directly transferred for silica gel chromatography.

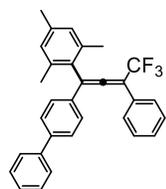
Characterization data for allenes



1-Mesityl-1,3-diphenyl-4,4,4-trifluoro-1,2-butadiene (1a) was prepared according to general procedure B from 1,1,1-trifluoro-2,4-diphenylbut-3-yn-2-ol (100 mg, 0.363 mmol) and mesitylene (253 μ L, 1.82 mmol, 5.0 equiv) with 5.9 mg (0.036 mmol) of FeCl₃ in 0.73 mL of HFIP. The reaction mixture was stirred at ambient temperature for 10 min. Purification by flash column chromatography over silica (petroleum ether) gave 128 mg (93% yield) of white solid. R_f = 0.83 (petroleum ether/EtOAc 9:1). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.49 (d, J = 7.5 Hz, 2H), 7.43–7.12 (m, 8H), 6.94 (s, 2H), 2.32 (s, 3H), 2.17 (s, 6H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ (ppm) 205.1 (q, J = 3.5 Hz), 138.1, 137.1, 133.3, 130.2, 129.9, 129.2, 128.9, 128.7, 128.6, 128.5, 127.6, 126.7, 123.7 (q, J = 275.1 Hz), 114.1, 104.0 (q, J = 34.3 Hz), 21.2, 20.4. ¹⁹F NMR (376.5 MHz, CDCl₃, CF₃COOH - ext. st.): δ (ppm) –62.5 (s, 3F). HRMS (APPI⁺-Orbitrap) m/z : [M]⁺. Calcd for C₂₅H₂₁F₃ 378.1590; Found 378.1596 (1.5 ppm).

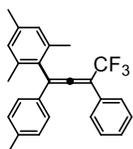


1-Cyclohexyl-1-mesityl-3-phenyl-4,4,4-trifluoro-1,2-butadiene (1b) was prepared according to general procedure B from 4-cyclohexyl-1,1,1-trifluoro-2-phenylbut-3-yn-2-ol (49 mg, 0.17 mmol) and mesitylene (70 μ L, 0.50 mmol, 3.0 equiv) with 2.7 mg (0.017 mmol) of FeCl₃, in 0.33 mL of HFIP. The reaction mixture was stirred at 50 °C for 24 h. Purification by flash column chromatography over silica (petroleum ether) gave 33 mg (51% yield) of the product. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.48 (d, J = 7.8 Hz, 2H), 7.37 (t, J = 7.7 Hz, 2H), 7.30 (t, J = 7.2 Hz, 1H), 6.89 (s, 2H), 2.41-2.15 (m, 10H), 2.03-1.91 (m, 2H), 1.87-1.75 (m, 2H), 1.75-1.66 (m, 1H), 1.43-1.18 (m, 5H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ (ppm) 201.5 (q, J = 4.0 Hz), 137.2, 131.9, 130.9, 128.7, 128.0, 127.32, 127.31, 124.1 (q, J = 272.7 Hz), 118.1, 102.2 (q, J = 33.8 Hz), 43.4, 32.1, 31.9, 26.7, 26.7, 26.2, 21.1. ¹⁹F NMR (376.5 MHz, CDCl₃): δ (ppm) –58.1 (s, 3F). HRMS (APPI⁺-Orbitrap) m/z : [M]⁺. Calcd for C₂₅H₂₇F₃ 384.2059; Found 384.2059 (–0.1 ppm).

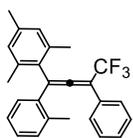


1-Mesityl-1-(1,1'-biphenyl-4-yl)-4,4,4-trifluoro-3-phenyl-1,2-butadiene (1c) was prepared according to general procedure B from 4-((1,1'-biphenyl-4-yl)-1,1,1-trifluoro-2-phenylbut-3-yn-2-ol (59 mg, 0.17 mmol) and mesitylene (71 μ L, 0.51 mmol, 3.0 equiv) with 2.7 mg (0.017 mmol) of FeCl₃, in 0.34 mL of HFIP. The reaction mixture was stirred at ambient temperature for 10 min. Purification by flash column chromatography over silica (petroleum ether) gave 31 mg (40% yield) of the product with 95% purity (the rest is the corresponding indene that started to form quickly). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.67-7.56 (m, 4H), 7.54 (d, J = 7.5 Hz, 2H), 7.46 (t, J = 7.5

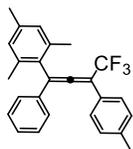
Hz, 2H), 7.43-7.30 (m, 6H), 6.99 (s, 2H), 2.36 (s, 3H), 2.23 (s, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ (ppm) 205.3 (q, $J = 3.9$ Hz), 141.5, 140.6, 138.1, 137.2, 132.2, 130.2, 129.9, 129.0, 128.9, 128.8, 128.6, 127.9, 127.7, 127.7, 127.2, 127.1, 123.7 (q, $J = 273.3$ Hz), 113.9, 104.1 (q, $J = 34.1$ Hz), 21.2, 20.4. ^{19}F NMR (376.5 MHz, CDCl_3): δ (ppm) -58.1 (s, 3F). HRMS (APPI⁺-Orbitrap) m/z : $[\text{M}]^+$. Calcd for $\text{C}_{31}\text{H}_{25}\text{F}_3$ 454.1903; Found 454.1903 (0.1 ppm).



1-Mesityl-4,4,4-trifluoro-1-(p-tolyl)-3-phenyl-1,2-butadiene (1d) was prepared according to general procedure B from 1,1,1-trifluoro-2-phenyl-4-(p-tolyl)but-3-yn-2-ol (85 mg, 0.29 mmol) and mesitylene (117 μL , 0.84 mmol, 5.0 equiv) with 4.6 mg (0.028 mmol) of FeCl_3 , in 0.57 mL of HFIP. The reaction mixture was stirred at ambient temperature for 10 min. Purification by flash column chromatography over silica (petroleum ether) gave 84 mg (74% yield) of the product. ^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.63 (d, $J = 7.6$ Hz, 2H), 7.50-7.31 (m, 3H), 7.33-7.22 (m, 4H), 7.07 (s, 2H), 2.46 (s, 3H), 2.44 (s, 3H), 2.32 (6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ (ppm) 205.0 (q, $J = 4.0$ Hz), 138.7, 138.0, 137.1, 130.4, 130.3, 130.0, 128.9, 128.7, 128.5, 127.6, 127.1, 126.1, 123.8 (q, $J = 273.5$ Hz), 114.1, 103.9 (q, $J = 34.2$ Hz), 21.4, 21.2, 20.4. ^{19}F NMR (376.5 MHz, CDCl_3): δ (ppm) -59.2 (s, 3F). HRMS (APPI⁺-Orbitrap) m/z : $[\text{M}]^+$. Calcd for $\text{C}_{26}\text{H}_{23}\text{F}_3$ 392.1746; Found 392.1750 (1.0 ppm).

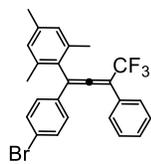


1-Mesityl-3-phenyl-3-(2-tolyl)-4,4,4-trifluoro-1,2-butadiene (1e) was prepared according to general procedure B from 1,1,1-trifluoro-4-phenyl-2-(o-tolyl)but-3-yn-2-ol (91 mg, 0.31 mmol) and mesitylene (188 μL , 1.57 mmol, 5.0 equiv) with 5.1 mg (0.031 mmol) of FeCl_3 , in 0.63 mL of HFIP. The reaction mixture was stirred at ambient temperature for 10 min. Purification by flash column chromatography over silica (petroleum ether) gave 118 mg (96% yield) of white solid. $R_f = 0.87$ (petroleum ether/EtOAc 9:1). ^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.52 (d, $J = 7.6$ Hz, 2H), 7.46-7.33 (m, 3H), 7.33-7.23 (m, 2H), 7.16 (t, $J = 7.6$ Hz, 1H), 7.00 (s, 2H), 6.91 (d, $J = 7.8$ Hz, 1H), 2.54 (s, 3H), 2.39 (s, 3H), 2.24 (s, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ (ppm) 205.4 (q, $J = 4.3$ Hz), 137.8, 137.6, 136.9, 132.6, 132.3, 131.7, 130.7, 128.9, 128.8, 128.4, 128.3, 128.2, 128.0, 126.5, 123.8 (q, $J = 274.6$ Hz), 112.5, 101.5 (q, $J = 34.5$ Hz), 22.0, 21.2, 20.4. ^{19}F NMR (376.5 MHz, CDCl_3 , CF_3COOH -ext. st.): δ (ppm) -58.2 (s, 3F). HRMS (APPI⁺-Orbitrap) m/z : $[\text{M}]^+$. Calcd for $\text{C}_{26}\text{H}_{23}\text{F}_3$ 392.1746; Found 392.1747 (0.2 ppm).

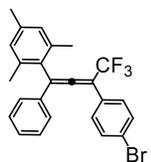


1-Mesityl-1-phenyl-3-tolyl-4,4,4-trifluoro-1,2-butadiene (1f) was prepared according to general procedure B from 1,1,1-trifluoro-4-phenyl-2-(p-tolyl)but-3-yn-2-ol (100 mg, 0.346 mmol) and mesitylene (241 μL , 1.73 mmol, 5.0 equiv) with 3.5 mg (0.022 mmol) of FeCl_3 , in 0.69 mL of HFIP. The reaction mixture was stirred at ambient temperature for 10 min. Purification by flash column chromatography over silica (petroleum ether) gave 122 mg (93% yield) of a colorless oil. $R_f = 0.93$ (petroleum ether/EtOAc 9:1). ^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.43 (d, $J = 8.0$ Hz, 2H), 7.40-7.32 (m, 3H), 7.32-7.27 (m, 2H), 7.21 (d, $J = 8.0$, 2H), 7.00 (s, 2H), 2.39 (s, 3H), 2.37 (s, 3H), 2.23 (s, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ (ppm) 204.8 (q, $J = 3.8$ Hz), 138.5, 138.0, 137.1, 133.4, 129.6, 129.1, 128.7, 128.5, 127.5, 127.1, 127.1, 126.7, 123.8 (q, $J = 275.2$ Hz), 113.9, 103.8 (q, J

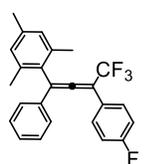
= 34.3 Hz), 21.3, 21.2, 20.4. ^{19}F NMR (376.5 MHz, CDCl_3 , CF_3COOH -ext. st.): δ (ppm) -58.3 (s, 3F). HRMS (APPI⁺-Orbitrap) m/z : $[\text{M}]^+$. Calcd for $\text{C}_{26}\text{H}_{23}\text{F}_3$ 392.1746; Found 392.1744 (-0.6 ppm).



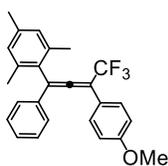
1-(4-Bromophenyl)-1-mesityl-3-phenyl-4,4,4-trifluoro-1,2-butadiene (1g) was prepared according to general procedure B from 4-(*p*-bromophenyl)-1,1,1-trifluoro-2-phenyl-but-3-yn-2-ol (86 mg, 0.24 mmol) and mesitylene (146 μL , 1.05 mmol, 5.0 equiv) with 3.4 mg (0.021 mmol) of FeCl_3 , in 0.5 mL of HFIP. The reaction mixture was stirred at ambient temperature for 10 min. Purification by flash column chromatography over silica (petroleum ether) gave 78 mg (70% yield) of a colorless oil. ^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.52-7.41 (m, 4H), 7.41-7.29 (m, 3H), 7.10 (d, $J = 8.6$ Hz, 2H), 6.95 (s, 2H), 2.32 (s, 3H), 2.15 (s, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ (ppm) 204.9 (q, $J = 3.8$ Hz), 138.3, 137.0, 132.3, 129.8, 129.3, 128.9, 128.8, 128.7, 128.1, 127.6, 127.6, 123.5 (q, $J = 273.5$ Hz), 122.7, 113.3, 104.3 (q, $J = 34.3$ Hz), 21.1, 20.3. ^{19}F NMR (376.5 MHz, CDCl_3 , C_6F_6 -ext. st.): δ (ppm) -62.5 (s, 3F). HRMS (APPI⁺-Orbitrap) m/z : $[\text{M}]^+$. Calcd for $\text{C}_{25}\text{H}_{20}^{79}\text{BrF}_3$ 456.0695; Found 456.0700 (1.1 ppm).



3-(4-Bromophenyl)-1-mesityl-1,3-diphenyl-4,4,4-trifluoro-1,2-butadiene (1h) was prepared according to general procedure B from 4-(4-bromophenyl)-1,1,1-trifluoro-2,4-diphenylbut-3-yn-2-ol (100 mg, 0.286 mmol) and mesitylene (199 μL , 1.43 mmol, 5.0 equiv) with 4.3 mg (0.029 mmol) of FeCl_3 , in 0.57 mL of HFIP. The reaction mixture was stirred at ambient temperature for 10 min. Purification by flash column chromatography over silica (petroleum ether) gave 118 mg (90% yield) of a colorless oil. $R_f = 0.82$ (petroleum ether/EtOAc 9:1). ^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.49 (d, $J = 8.6$ Hz, 2H), 7.38-7.28 (m, 5H), 7.25-7.18 (m, 2H), 6.95 (s, 2H), 2.33 (s, 3H), 2.16 (s, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ (ppm) 205.0 (q, $J = 3.8$ Hz), 138.2, 137.0, 132.9, 132.1, 129.6, 129.3, 129.2, 129.2, 128.8, 127.1, 126.7, 123.5 (q, $J = 275.0$ Hz), 122.7, 114.6, 103.2 (q, $J = 34.6$ Hz), 21.2, 20.4. ^{19}F NMR (376.5 MHz, CDCl_3 , C_6F_6 -ext. st.): δ (ppm) -62.5 (s, 3F). HRMS (APPI⁺-Orbitrap) m/z : $[\text{M}]^+$. Calcd for $\text{C}_{25}\text{H}_{20}^{79}\text{BrF}_3$ 456.0695; Found 456.0699 (0.9 ppm).

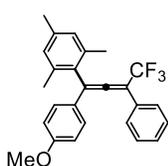


3-(4-Fluorophenyl)-1-mesityl-1-phenyl-4,4,4-trifluoro-1,2-butadiene (1i) was prepared according to modified general procedure B from 1,1,1-trifluoro-2-(*p*-fluorophenyl)-4-phenyl-but-3-yn-2-ol (72 mg, 0.21 mmol) and mesitylene (146 μL , 1.05 mmol, 5.0 equiv) with 3.4 mg (0.021 mmol) of FeCl_3 , in 0.42 mL of HFIP. The reaction mixture was stirred at ambient temperature for 1 h. Purification by flash column chromatography over silica (petroleum ether) gave 50 mg (52% yield) of white solid. ^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.56-7.48 (m, 2H), 7.44-7.33 (m, 3H), 7.33-7.27 (m, 2H), 7.16-7.07 (m, 2H), 7.02 (s, 2H), 2.39 (s, 3H), 2.23 (s, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ (ppm) 204.8 (q, $J = 3.6$ Hz), 162.9 (d, $J = 246.9$ Hz), 138.2, 137.0, 133.1, 129.7, 129.5 (d, $J = 8.1$ Hz), 129.2, 128.8, 128.7, 126.6, 126.2 (d, $J = 3.3$ Hz), 123.6 (q, $J = 273.3$ Hz), 116.1 (d, $J = 21.7$ Hz), 114.3, 103.1 (q, $J = 34.6$ Hz), 21.3, 20.3. ^{19}F NMR (376.5 MHz, CDCl_3 , C_6F_6 -ext. st.): δ (ppm) -62.8 (s, 3F), -116.0 (m, 1F). HRMS (APPI⁺-Orbitrap) m/z : $[\text{M}]^+$. Calcd for $\text{C}_{25}\text{H}_{20}\text{F}_4$ 396.1496; Found 396.1500 (1.0 ppm).



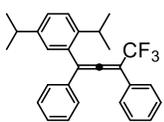
1-Mesityl-3-(4-methoxyphenyl)-1-phenyl-trifluoro-1,2-butadiene (**1j**) was prepared according to modified general procedure B from 1,1,1-trifluoro-2-(4-methoxyphenyl)-4-phenylbut-3-yn-2-ol (71 mg, 0.25 mmol) and mesitylene (102 μ L, 0.735 mmol, 3.0 equiv) with 4.0 mg (0.025 mmol) of FeCl_3 , in 0.98 mL of HFIP. The reaction mixture was stirred at ambient temperature for 10 min.

Purification by flash column chromatography over silica (petroleum ether/EtOAc 40:1 to 30:1) gave 79 mg (82% yield) of colorless oil. $R_f = 0.81$ (petroleum ether/EtOAc 9:1). ^1H NMR (500 MHz, CDCl_3): δ (ppm) 7.42 (d, $J = 8.5$ Hz, 2H), 7.38–7.21 (m, 5H), 6.96 (s, 2H), 6.90 (d, $J = 8.8$ Hz, 2H), 3.82 (s, 3H), 2.34 (s, 3H), 2.18 (s, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ (ppm) 204.5 (q, $J = 3.5$ Hz), 159.8, 138.0, 137.1, 133.5, 130.1, 129.1, 128.9, 128.7, 128.5, 126.6, 123.8 (q, $J = 275.0$ Hz), 122.2, 114.3, 113.8, 103.6 (q, $J = 34.5$ Hz), 55.4, 21.2, 20.4. ^{19}F NMR (376.5 MHz, CDCl_3 , CF_3COOH -ext. st.): δ (ppm) -59.1 (s, 3F). HRMS (APPI⁺-Orbitrap): m/z $[\text{M}]^+$. Calcd for $\text{C}_{26}\text{H}_{23}\text{F}_3\text{O}$ 408.1696; Found 408.1708 (2.9 ppm).



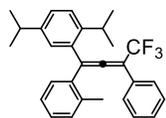
1-Mesityl-4-(4-methoxyphenyl)-3-phenyl-4,4,4-trifluoro-1,2-butadiene (**1k**) was prepared according to modified general procedure B from 1,1,1-trifluoro-4-(4-methoxyphenyl)-2-phenylbut-3-yn-2-ol (73 mg, 0.24 mmol) and mesitylene (84 μ L, 0.74 mmol, 2.5 equiv) with 3.9 mg (0.024 mmol) of FeCl_3 , in 0.48 mL of HFIP. The reaction mixture was stirred at ambient temperature for 10 min. Purification

by flash column chromatography over silica gave 26 mg (27% yield) of the product. ^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.50 (d, $J = 7.6$ Hz, 2H), 7.41–7.29 (m, 3H), 7.20 (d, $J = 8.8$ Hz, 2H), 6.95 (s, 2H), 6.88 (d, $J = 8.8$ Hz, 2H), 3.82 (s, 3H), 2.33 (s, 3H), 2.19 (s, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ (ppm) 204.8 (q, $J = 3.9$ Hz), 160.0, 137.9, 137.1, 130.5, 130.1, 128.8, 128.7, 128.4, 128.0, 127.6, 127.6, 125.3, 123.7 (q, $J = 273.3$ Hz), 114.6, 113.7, 103.8 (q, $J = 34.1$ Hz), 55.5, 21.2, 20.3. ^{19}F NMR (376.5 MHz, CDCl_3): δ (ppm) -59.3 (s, 3F). HRMS (APPI⁺-Orbitrap) m/z : $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{26}\text{H}_{24}\text{F}_3\text{O}$ 409.1774; found 409.1768 (-1.5 ppm).

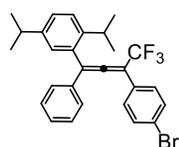


1-(2,5-Diisopropylphenyl)-1,3-diphenyl-4,4,4-trifluoro-1,2-butadiene (**1l**) was prepared according to general procedure B from 1,1,1-trifluoro-2,4-diphenylbut-3-yn-2-ol (104 mg, 0.376 mmol) and diisopropyl benzene (356 μ L, 1.88 mmol, 5.0 equiv) with 6.1 mg (0.038 mmol) of FeCl_3 , in 0.75 mL of HFIP. The reaction

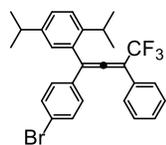
mixture was stirred at ambient temperature for 10 min. Purification by flash column chromatography over silica (petroleum ether) gave 103 mg (65% yield) of a colorless oil. $R_f = 0.82$ (petroleum ether/EtOAc 9:1). ^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.45 (d, $J = 7.9$ Hz, 2H), 7.35–7.27 (m, 2H), 7.25–7.14 (m, 8H), 7.20–7.12 (m, 1H), 2.94 (sept, $J = 6.8$ Hz, 1H), 2.83 (sept, $J = 6.9$ Hz, 1H), 1.18 (d, $J = 6.9$ Hz, 6H), 1.04 (d, $J = 6.8$ Hz, 3H), 0.94 (d, $J = 6.9$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ (ppm) 205.5 (q, $J = 3.6$ Hz), 146.7, 145.0, 134.7, 132.0, 130.1, 128.9, 128.9, 128.5, 128.5, 128.3, 127.3, 127.3, 127.2, 126.2, 123.6 (q, $J = 273.6$ Hz), 116.4, 103.9 (q, $J = 34.1$ Hz), 33.7, 30.4, 24.4, 24.1, 24.1, 24.1. ^{19}F NMR (376.5 MHz, CDCl_3 , CF_3COOH -ext. st.): δ (ppm) -58.7 (s, 3F). HRMS (APPI⁺-Orbitrap) m/z $[\text{M}]^+$. Calcd for $\text{C}_{28}\text{H}_{27}\text{F}_3$ 420.2059; Found 420.2062 (0.7 ppm).



1-(2,5-Diisopropylphenyl)-3-phenyl-3-(2-tolyl)-4,4,4-trifluoro-1,2-butadiene (1m) was prepared according to modified general procedure B from 1,1,1-trifluoro-4-phenyl-2-(*o*-tolulyl)but-3-yn-2-ol (63 mg, 0.22 mmol) and diisopropylbenzene (123 μ L, 0.647 mmol, 3.0 equiv) with 3.5 mg (0.022 mmol) of FeCl₃, in 0.86 mL of HFIP. The reaction mixture was stirred at ambient temperature for 3 h. Purification by flash column chromatography over silica (petroleum ether) gave 63 mg (58% yield) of colorless oil. R_f = 0.84 (petroleum ether/EtOAc 9:1). ¹H NMR (500 MHz, CDCl₃): δ (ppm) 7.49 (d, J = 7.7 Hz, 2H), 7.41–7.34 (m, 2H), 7.34–7.28 (m, 2H), 7.23 (d, J = 2.0 Hz, 1H), 7.21 (d, J = 4.0 Hz, 2H) 7.18–7.13 (m, 1H), 7.11 (d, J = 1.7 Hz, 1H), 7.03 (d, J = 7.6 Hz, 1H), 3.00 (sept, J = 6.8 Hz, 1H), 2.87 (sept, J = 6.9 Hz, 1H) 2.30 (s, 3H), 1.30–1.16 (d, J = 7.0 Hz, 6H), 1.04 (d, J = 6.9 Hz, 3H), 1.02 (d, J = 6.9 Hz, 3H). ¹³C {¹H} NMR (125 MHz, CDCl₃): δ (ppm) 205.7 (q, J = 3.6 Hz), 146.6, 144.8, 137.0, 134.7, 134.0, 131.3, 130.6, 129.7, 128.8, 128.3, 128.3, 128.2, 127.4 (q, J = 1.1 Hz), 127.0, 126.3, 126.2, 123.8 (q, J = 274.8 Hz), 115.2, 101.4 (q, J = 34.1 Hz), 33.6, 30.0, 24.2, 24.1, 21.5. ¹⁹F NMR (282 MHz, CDCl₃, CF₃COOH-ext. st.): δ (ppm) –60.5 (s, 3F). HRMS (APPI⁺-Obitrap) m/z : [M]⁺. Calcd for C₂₉H₂₉F₃ 434.2216; Found 434.2226 (2.3 ppm).

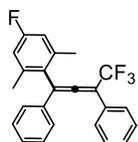


1-(4-Bromophenyl)-1-(2,5-diisopropylphenyl)-3-phenyl-4,4,4-trifluoro-1,2-butadiene (1n) was prepared according to general procedure B from 4-(4-bromophenyl)-1,1,1-trifluoro-2,4-diphenylbut-3-yn-2-ol (10.2 mg, 0.28 mmol) and diisopropylbenzene (267 μ L, 1.411 mmol, 5.0 equiv) with 4.5 mg (0.028 mmol) of FeCl₃, in 0.56 mL of HFIP. The reaction mixture was stirred at ambient temperature for 10 min. Purification by flash column chromatography over silica (petroleum ether) gave 56 mg (40% yield) of yellow solid. R_f = 0.87 (petroleum ether/EtOAc 9:1). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.55–7.47 (m, 2H), 7.44–7.28 (m, 7H), 7.25–7.19 (m, 2H), 7.14–7.08 (m, 1H), 2.98 (sept, J = 6.8 Hz, 1H), 2.90 (sept, J = 6.9 Hz, 1H), 1.25 (d, J = 6.9 Hz, 6H), 1.12 (d, J = 6.8 Hz, 3H), 1.00 (d, J = 6.8 Hz, 3H). ¹³C {¹H} NMR (125 MHz, CDCl₃): δ (ppm) 205.4 (q, J = 4.2 Hz), 146.8, 145.0, 134.3, 132.1, 131.7, 129.1, 129.0, 128.8, 128.7, 128.2, 127.4, 127.3, 126.3, 123.3 (q, J = 275.0 Hz), 122.7, 117.0, 103.1 (q, J = 34.8 Hz), 33.7, 30.4, 24.4, 24.1. ¹⁹F NMR (376.5 MHz, CDCl₃, CF₃COOH-ext. st.): δ (ppm) –58.8 (s, 3F). HRMS (APPI⁺-Orbitrap) m/z : [M]⁺. Calcd for C₂₈H₂₆⁷⁹BrF₃ 498.1165; Found 498.1168 (0.6 ppm).

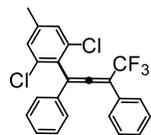


1-(4-Bromophenyl)-1-(2,5-diisopropylphenyl)-3-phenyl-4,4,4-trifluoro-1,2-butadiene (1o) was prepared according to general procedure B from 4-(4-bromophenyl)-1,1,1-trifluoro-2-phenylbut-3-yn-2-ol (111 mg, 0.314 mmol) and diisopropylbenzene (297 μ L, 1.568 mmol, 5.0 equiv) with 4.7 mg (0.031 mmol) of FeCl₃, in 0.63 mL of HFIP. The reaction mixture was stirred at ambient temperature for 3 h. Purification by flash column chromatography over silica (petroleum ether) gave 111 mg (70% yield) of a colorless oil. R_f = 0.88 (petroleum ether/EtOAc 9:1). ¹H NMR (500 MHz, CDCl₃): δ (ppm) 7.52 (d, J = 7.7 Hz, 2H), 7.47 (d, J = 8.6 Hz, 2H), 7.42–7.36 (m, 2H), 7.36–7.31 (m, 2H), 7.31–7.27 (m, 1H), 7.15–7.10 (m, 3H), 2.98 (sept, J = 6.9 Hz, 1H), 2.92 (sept, J = 6.9 Hz, 1H), 1.26 (d, J = 6.9 Hz, 6H), 1.13 (d, J = 6.8 Hz, 3H), 1.03 (d, J = 6.9 Hz, 3H). ¹³C {¹H} NMR (125 MHz, CDCl₃): δ (ppm) 206.3 (q, J = 3.9 Hz), 146.9, 145.0, 133.8, 132.1, 131.6, 129.7, 129.0, 128.8, 128.7, 128.2, 127.5, 127.3, 126.3, 123.4 (q, J = 273.5 Hz), 122.7, 115.7, 104.3 (q, J = 34.2

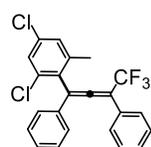
Hz), 33.7, 30.4, 24.4, 24.1, 24.1, 24.1. ^{19}F NMR (282 MHz, CDCl_3 , CF_3COOH -ext. st.): δ (ppm) -60.8 (s, 3F). HRMS (APPI $^+$ -Orbitrap) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{28}\text{H}_{26}^{79}\text{BrF}_3$ 498.1165; Found 498.1175 (2.0 ppm).



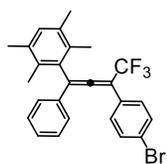
1-(2-(5-Fluoro-m-xylenyl))-1,3-diphenyl-4,4,4-trifluoro-1,2-butadiene (1p) was prepared according to modified general procedure B from 1,1,1-trifluoro-2,4-diphenylbut-3-yn-2-ol (104 mg, 0.376 mmol) and 5-fluoro-*m*-xylene (142 μL , 1.13 mmol, 3.0 equiv) with 6.1 mg (0.038 mmol) of FeCl_3 , in 1.50 mL of HFIP. The reaction mixture was heated at 80 $^\circ\text{C}$ for 24 h. Purification by flash column chromatography over silica (petroleum ether) gave 37 mg (25% yield) of colorless oil. $R_f = 0.84$ (petroleum ether/EtOAc 9:1). ^1H NMR (500 MHz, CDCl_3): δ (ppm) 7.48 (d, $J = 7.4$ Hz, 2H), 7.40–7.29 (m, 6H), 7.25–7.20 (m, 2H), 6.84 (d, $J = 9.4$ Hz, 2H), 2.20 (s, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ (ppm) 205.1 (q, $J = 3.8$ Hz), 162.4 (d, $J = 244.7$ Hz), 139.7 (d, $J = 7.2$ Hz), 132.9, 129.9, 129.3, 129.0, 128.8, 128.7, 128.6 (d, $J = 2.0$ Hz), 127.6 (q, $J = 1.1$ Hz), 126.6, 123.6 (q, $J = 273.5$ Hz), 114.6 (d, $J = 21.0$ Hz), 113.5, 104.3 (q, $J = 34.3$ Hz), 20.6. ^{19}F NMR (282 MHz, CDCl_3 , CF_3COOH -ext. st.): δ (ppm) -60.1 (s, 3F), -115.9 (s, 1H). HRMS (APPI $^+$ -Orbitrap) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{24}\text{H}_{18}\text{F}_4$ 382.1339; Found 382.1348 (2.4 ppm).



1-(2,6-Dichloro-4-methylphenyl)-1,3-diphenyl-4,4,4-trifluoro-1,2-butadiene (1q) was prepared according to modified general procedure B from 1,1,1-trifluoro-2,4-diphenylbut-3-yn-2-ol (108 mg, 0.392 mmol) and 3,5-dichlorotoluene (190 mg, 1.18 mmol, 3.0 equiv) with 6.4 mg (0.039 mmol) of FeCl_3 , in 1.57 mL of HFIP. The reaction mixture was heated at 80 $^\circ\text{C}$ for 24 h. Purification by flash column chromatography over silica (petroleum ether) gave 31 mg (23% yield) of white solid. ^1H NMR (500 MHz, CDCl_3): δ (ppm) 7.56 (d, $J = 7.1$ Hz, 2H), 7.41–7.30 (m, 7H), 7.24–7.19 (m, 3H), 2.27 (s, 3H). 7.56 (d, $J = 7.1$ Hz, 2H), 7.41–7.30 (m, 7H), 7.24–7.19 (m, 3H), 2.27 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ (ppm) 205.3 (q, $J = 3.9$ Hz), 141.1, 135.3, 134.7, 132.1, 131.0, 129.3, 129.1, 129.0, 128.9, 127.7 (q, $J = 1.2$ Hz), 127.3, 126.5, 123.4 (q, $J = 273.9$ Hz), 112.8, 106.6 (q, $J = 34.2$ Hz), 20.6. ^{19}F NMR (282 MHz, CDCl_3 , CF_3COOH -ext. st.): δ (ppm) -60 . (s, 3F). HRMS (APPI $^+$ -Orbitrap) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{23}\text{H}_{15}\text{Cl}_2\text{F}_3$ 418.0497; Found 418.0500 (0.7 ppm).



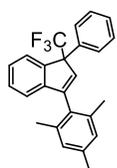
1-(2,4-Dichloro-5-methylphenyl)-1,3-diphenyl-4,4,4-trifluoro-1,2-butadiene (1q') was prepared according to modified general procedure B from 1,1,1-trifluoro-2,4-diphenylbut-3-yn-2-ol (108 mg, 0.392 mmol) and 3,5-dichlorotoluene (190 mg, 1.18 mmol, 3.0 equiv) with 6.4 mg (0.039 mmol) of FeCl_3 , in 1.57 mL of HFIP. The reaction mixture was heated at 80 $^\circ\text{C}$ for 24 h. Purification by flash column chromatography over silica (petroleum ether) gave 17 mg (10% yield) of white solid. ^1H NMR (500 MHz, CDCl_3) δ (ppm) 7.57 (d, $J = 7.1$ Hz, 2H), 7.43 – 7.31 (m, 7H), 7.25 – 7.20 (m, 3H), 2.27 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ (ppm) 205.3 (q, $J = 3.9$ Hz), 141.1, 135.3, 134.7, 132.1, 131.0, 129.3, 129.1, 129.0, 128.9, 127.7 (q, $J = 1.2$ Hz), 127.3, 126.5, 123.4 (q, $J = 273.9$ Hz), 112.8, 106.6 (q, $J = 34.2$ Hz), 20.6. ^{19}F NMR (282 MHz, CDCl_3 , CF_3COOH -ext. st.): δ (ppm) -60.8 (s, 3F). HRMS (APPI $^+$ -Orbitrap) m/z $[\text{M}]^+$ Calcd for $\text{C}_{23}\text{H}_{15}\text{Cl}_2\text{F}_3$ 418.0497; Found 418.0500 (0.7 ppm).



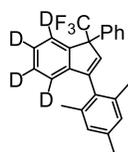
3-(4-Bromophenyl)-1-durenyl-1,3-diphenyl-4,4,4-trifluoro-1,2-butadiene (1s) was prepared according to modified general procedure B 4-(4-bromophenyl)-1,1,1-trifluoro-2,4-diphenylbut-3-yn-2-ol (101 mg, 0.284 mmol) and durene (114 mg, 0.85 mmol, 3.0 equiv.) with 2.9 mg (0.028 mmol) of FeCl₃ in 1.13 mL of HFIP.

The reaction mixture was heated at 80 °C for 3 h. Purification by flash column chromatography over silica (petroleum ether) gave 125 mg (93% yield) of white solid. $R_f = 0.90$ (petroleum ether/EtOAc 9:1). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.49 (dd, $J = 8.8, 2.0$ Hz, 2H), 7.39–7.30 (m, 5H), 7.24–7.17 (m, 2H), 7.03 (s, 1H), 2.26 (s, 3H), 2.24 (s, 3H), 2.14 (s, 3H), 2.06 (s, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ (ppm) 205.0 (q, $J = 3.6$ Hz), 134.6, 134.2, 133.2, 132.6, 132.5, 132.1, 131.7, 129.4, 129.2, 128.8, 126.9, 123.6 (q, $J = 275.2$ Hz), 122.7, 115.8, 103.2 (q, $J = 34.8$ Hz), 20.2 (2C), 17.5, 16.7. ¹⁹F NMR (376.5 MHz, CDCl₃, CF₃COOH-ext. st.): δ (ppm) –59.0 (s, 3F). HRMS (APPI⁺-Orbitrap) m/z : [M]⁺. Calcd for C₂₆H₂₂⁷⁹BrF₃ 470.0851; Found 470.0862 (2.3 ppm).

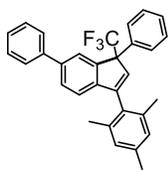
Characterization data for indenenes



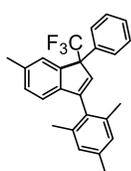
3-Mesityl-1-phenyl-1-(trifluoro-methyl)-1H-indene (2a) was prepared according to general procedure C from 1,1,1-trifluoro-2,4-diphenylbut-3-yn-2-ol (106 mg, 0.382 mmol) and mesitylene (160 μL, 1.15 mmol, 3.0 equiv) with 6.2 mg (0.038 mmol) of FeCl₃ in 1.50 mL of HFIP. The reaction mixture was heated at 80 °C for 24 h. Purification by flash column chromatography over silica (petroleum ether) gave 137 mg (94% yield) of a colorless oil. $R_f = 0.80$ (petroleum ether/EtOAc 9:1). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.68–7.61 (m, 1H), 7.61–7.55 (m, 2H), 7.38–7.29 (m, 5H), 6.98 (s, 1H), 6.94 (s, 1H), 6.93–6.90 (m, 1H), 6.44 (s, 1H), 2.35 (s, 3H), 2.15 (s, 3H), 2.05 (s, 3H). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ (ppm) 147.1, 145.0, 143.5, 137.6, 136.9, 136.5, 135.0, 133.4, 130.5, 128.9, 128.8, 128.4, 128.2, 128.1, 127.8, 126.9 (q, $J = 280.6$ Hz), 126.7, 125.4, 121.4, 64.8 (q, $J = 26.6$ Hz), 21.3, 20.3, 20.0. ¹⁹F NMR (282 MHz, CDCl₃, CF₃COOH-ext. st.): δ (ppm) –68.2 (s, 3F). HRMS (APPI⁺-Orbitrap) m/z : [M]⁺. Calcd for C₂₅H₂₁F₃ 378.1590; Found 378.1593 (0.8 ppm).



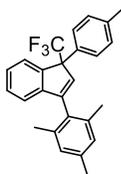
4,5,6,7-Tetradeutero-3-mesityl-1-phenyl-1-(trifluoro-methyl)-1H-indene (2a-d₄) was prepared according to general procedure C from 1,1,1-trifluoro-2-phenyl-4-pentadeuterophenyl-but-3-yn-2-ol (68.4 mg, 0.243 mmol) and mesitylene (102 μL, 0.73 mmol, 3.0 equiv) with 3.9 mg (0.024 mmol) of FeCl₃ in 0.97 mL of HFIP. The reaction mixture was heated at 80 °C for 24 h. Purification by flash column chromatography over silica (petroleum ether) gave 37 mg (39% yield) of a colorless oil. $R_f = 0.80$ (petroleum ether/EtOAc 9:1). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.62–7.56 (m, 2H), 7.41–7.29 (m, 3H), 6.99 (s, 1H), 6.95 (s, 1H), 6.45 (s, 1H), 2.36 (s, 3H), 2.17 (s, 3H), 2.07 (s, 3H). ²H NMR (600 MHz, CH₂Cl₂): δ (ppm) 7.71 (br. s, 1D), 7.38 (br. s, 2D), 6.94 (br. s, 1D). HRMS (ESI-TOF) m/z : [M+H]⁺. Calcd for C₂₅H₁₈D₄F₃ 383.1919; Found 383.1918 (0.3 ppm).



3-Mesityl-1,6-diphenyl-1-(trifluoromethyl)-1H-indene (2c) was prepared according to modified general procedure C from 4-((1,1'-biphenyl)-4-yl)-1,1,1-trifluoro-2-phenylbut-3-yn-2-ol (70 mg, 0.20 mmol) and mesitylene (84 μ L, 0.60 mmol, 3.0 equiv) with 3.3 mg (0.020 mmol) of FeCl_3 , in 0.41 mL of HFIP. The reaction mixture was heated at 50 $^\circ\text{C}$ for 6 h. Purification by flash column chromatography over silica (petroleum ether) gave 82 mg (91% yield) of the product (in 90% purity). ^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.84 (s, 1H), 7.68-7.57 (m, 4H), 7.54 (dd, $J = 7.9$, 1.6 Hz, 1H), 7.47-7.40 (m, 2H), 7.38-7.30 (m, 4H), 7.03-6.93 (m, 3H), 6.46 (s, 1H), 2.35 (s, 3H), 2.18 (s, 3H), 2.09 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ (ppm) 146.9, 144.4, 144.2, 144.1, 140.1, 137.7, 136.9, 136.5, 135.0, 133.7, 130.5, 129.0, 128.9, 128.5, 128.3, 128.2, 128.0, 127.8, 127.5, 127.4, 126.9 (q, $J = 280.8$ Hz), 124.4, 121.6, 65.4 (q, $J = 26.6$ Hz), 21.3, 20.4, 20.1. ^{19}F NMR (376.5 MHz, CDCl_3): δ (ppm) -65.9 (s, 3F). HRMS (APPI⁺-Orbitrap) m/z $[\text{M}]^+$. Calcd for $\text{C}_{31}\text{H}_{25}\text{F}_3$ 454.1903; Found 454.1904 (0.2 ppm).



3-Mesityl-6-methyl-1-phenyl-1-(trifluoromethyl)-1H-indene (2d) was prepared according to modified general procedure C from 1,1,1-trifluoro-2-phenyl-4-(*p*-toluyl)but-3-yn-2-ol (80 mg, 0.28 mmol) and mesitylene (117 μ L, 0.84 mmol, 3.0 equiv) with 4.5 mg (0.028 mmol) of FeCl_3 , in 0.55 mL of HFIP. The reaction mixture was heated at 50 $^\circ\text{C}$ for 6 h. Purification by flash column chromatography over silica (petroleum ether) gave 98 mg (91% yield) of the product. ^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.65 (d, $J = 7.3$ Hz, 2H), 7.52 (s, 1H), 7.44-7.33 (m, 3H), 7.19 (d, $J = 7.7$ Hz, 1H), 7.04 (s, 1H), 7.00 (s, 1H), 6.88 (d, $J = 7.6$ Hz, 1H), 6.43 (s, 1H), 2.47 (s, 3H), 2.40 (s, 3H), 2.23 (s, 3H), 2.13 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ (ppm) 147.0, 143.9, 142.4, 137.5, 136.9, 136.7, 136.5, 135.3, 132.5, 130.7, 129.6, 128.8, 128.4, 128.2, 128.0, 127.8, 127.0 (q, $J = 280.9$ Hz), 126.3, 121.1, 64.7 (q, $J = 26.3$ Hz), 21.8, 21.2, 20.3, 20.0. ^{19}F NMR (376.5 MHz, CDCl_3): δ (ppm) -66.0 (s, 3F). HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{26}\text{H}_{24}\text{F}_3$ 393.1825; Found 393.1815 (2.5 ppm).



3-Mesityl-1-toluy-1-(trifluoromethyl)-1H-indene (2f) was prepared according to general procedure C from 1,1,1-trifluoro-4-phenyl-2-(*p*-toluyl)but-3-yn-2-ol (93 mg, 0.32 mmol) and mesitylene (133 μ L, 0.96 mmol, 3.0 equiv) with 5.1 mg (0.032 mmol) of FeCl_3 , in 1.27 mL of HFIP. The reaction mixture was stirred at ambient temperature for 3 h. Purification by flash column chromatography over silica (petroleum ether) gave 120 mg (96% yield) of colorless oil. $R_f = 0.83$ (petroleum ether/EtOAc 9:1). ^1H NMR (500 MHz, CDCl_3) δ (ppm) 7.67-7.64 (m, 1H), 7.48 (d, $J = 8.0$ Hz, 2H), 7.34-7.28 (m, 2H), 7.16 (d, $J = 8.1$ Hz, 2H), 6.99 (s, 1H), 6.95 (s, 1H), 6.93-6.90 (m, 1H), 6.44 (s, 1H), 2.35 (s, 3H), 2.34 (s, 3H), 2.16 (s, 3H), 2.06 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3) δ (ppm) 146.9, 144.9, 143.6, 137.9, 137.6, 136.9, 136.5, 133.5, 131.9, 130.6, 129.5, 128.8, 128.4, 128.2, 127.7, 126.9 (q, $J = 282.5$ Hz), 126.6, 125.4, 121.3, 64.5 (q, $J = 26.7$ Hz), 21.2, 21.1, 20.3, 20.0. ^{19}F NMR (376.5 MHz, CDCl_3 , C_6F_6 -ext. st.): δ (ppm) -68.4 (s, 3F). HRMS (APPI⁺-Orbitrap) m/z : $[\text{M}]^+$. Calcd for $\text{C}_{26}\text{H}_{23}\text{F}_3$ 392.1746; Found 392.1747 (0.3 ppm).



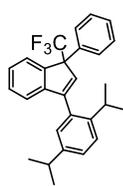
3-Mesityl-1-(4-methoxyphenyl)-1-(trifluoromethyl)-1H-indene (2j) was prepared according to modified general procedure C from 1,1,1-trifluoro-2-(4-methoxyphenyl)-4-phenylbut-3-yn-2-ol (109 mg, 0.356 mmol) and mesitylene (149 μ L, 1.07 mmol, 3.0 equiv) with 5.8 mg (0.036 mmol) of FeCl_3 , in 1.42 mL of HFIP.

The reaction mixture was heated at 80 $^\circ\text{C}$ for 1 h. Purification by flash column chromatography over silica (petroleum ether/EtOAc 40:1 to 30:1) gave 131 mg (90% yield) of yellow oil. $R_f = 0.58$ (petroleum ether/EtOAc 9:1). ^1H NMR (400 MHz, CDCl_3) δ ppm 7.69–7.63 (m, 1H), 7.54–7.48 (d, $J = 8.8$ Hz, 2H), 7.31 (dd, $J = 5.5, 3.1$ Hz, 2H), 6.98 (s, 1H), 6.94 (s, 1H), 6.91 (dd, $J = 5.5, 3.2$ Hz, 1H), 6.87 (d, $J = 8.9$ Hz, 2H), 6.43 (s, 1H), 3.80 (s, 3H), 2.35 (s, 3H), 2.15 (s, 3H), 2.04 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ (ppm) 159.3, 146.8, 144.9, 143.6, 137.6, 136.9, 136.5, 133.5, 130.6, 129.1, 128.8, 128.4, 128.2, 126.7, 126.9 (q, $J = 282.5$ Hz), 126.6, 125.4, 121.4, 114.1, 64.2 (q, $J = 26.8$ Hz), 55.4, 21.2, 20.3, 20.0. ^{19}F NMR (376.5 MHz, CDCl_3 , CF_3COOH -ext. st.): δ (ppm) –66.6 (s, 3F). HRMS (APPI $^+$ -Orbitrap) m/z : $[\text{M}]^+$. Calcd for $\text{C}_{26}\text{H}_{23}\text{F}_3\text{O}$ 408.1696; Found 408.1697 (0.2 ppm).



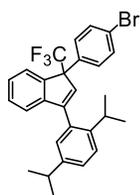
3-Mesityl-5-methoxy-1-phenyl-1-(trifluoromethyl)-1H-indene (2k) was prepared according to general procedure C from 1,1,1-trifluoro-4-methoxyphenyl-2-phenylbut-3-yn-2-ol (106 mg, 0.345 mmol) and mesitylene (144 μ L, 1.03 mmol, 3.0 equiv) with 5.6 mg (0.035 mmol) of FeCl_3 , in 1.03 mL of HFIP. The reaction mixture was heated at 80 $^\circ\text{C}$ for 24 h. Purification by flash column chromatography

over silica (petroleum ether/EtOAc 40:1 to 30:1) gave 84 mg (60% yield) of a colorless oil. $R_f = 0.74$ (petroleum ether/EtOAc 9:1). ^1H NMR (400 MHz, CDCl_3) δ 7.56 (d, $J = 7.8$ Hz, 2H), 7.35–7.25 (m, 3H), 7.19 (s, 1H), 6.95 (s, 1H), 6.91 (s, 1H), 6.80 (s, 2H), 6.28 (s, 1H), 3.78 (s, 3H), 2.31 (s, 3H), 2.14 (s, 3H), 2.06 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ (ppm) 159.1, 146.7, 145.4, 137.8, 137.5, 136.9, 136.5, 135.2, 131.4, 130.8, 128.8, 128.4, 128.2, 128.1, 127.7, 126.9 (q, $J = 282.5$ Hz), 121.8, 113.5, 112.7, 64.7 (q, $J = 26.7$ Hz), 55.7, 21.2, 20.3, 20.0. ^{19}F NMR (376.5 MHz, CDCl_3 , CF_3COOH -ext. st.): δ (ppm) –74.9 (s, 3F). HRMS (APPI $^+$ -Orbitrap) m/z : $[\text{M}]^+$. Calcd for $\text{C}_{26}\text{H}_{23}\text{F}_3\text{O}$ 408.1696; Found 408.1695 (–0.2 ppm).



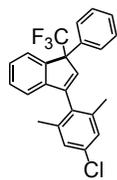
3-(2,5-Diisopropylphenyl)-1-phenyl-1-(trifluoromethyl)-1H-indene (2l) was prepared according to general procedure C from 1,1,1-trifluoro-2,4-diphenylbut-3-yn-2-ol (104 mg, 0.375 mmol) and diisopropyl benzene (213 μ L, 1.13 mmol, 3.00 equiv) with 6.1 mg (0.038 mmol) of FeCl_3 , in 0.75 mL of HFIP. The reaction mixture was stirred at ambient temperature for 3 h. Purification by flash column chromatography over silica

(petroleum ether) gave 142 mg (90% yield) of a white solid. $R_f = 0.91$ (petroleum ether/EtOAc 9:1). ^1H NMR (500 MHz, CDCl_3) δ (ppm) 7.37–7.20 (m, 11H), 7.17 (d, $J = 8.3$ Hz, 1H), 6.15 (s, 1H), 2.94–2.85 (m, 2H), 1.15 (d, $J = 6.8$ Hz, 3H), 1.00 (d, $J = 7.4$ Hz, 3H), 0.98 (d, $J = 7.4$ Hz, 3H), 0.66 (d, $J = 6.7$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ (ppm) 148.5, 143.7, 141.8, 141.1, 141.0, 138.1, 136.4 (q, $J = 2.1$ Hz), 134.8, 131.9, 128.7 (q, $J = 2.0$ Hz), 128.2, 128.1, 127.9, 127.8, 126.7, 126.8 (q, $J = 283.5$ Hz), 126.1, 125.7, 121.5, 64.4 (q, $J = 26.4$ Hz), 29.3, 27.1, 24.3, 23.9, 23.6, 23.4. ^{19}F NMR (376.5 MHz, CDCl_3 , CF_3COOH -ext. st.): δ (ppm) –63.7 (s, 3F). HRMS (APPI $^+$ -Orbitrap) m/z : $[\text{M}]^+$. Calcd for $\text{C}_{28}\text{H}_{27}\text{F}_3$ 420.2059; Found 420.2061 (1.9 ppm).



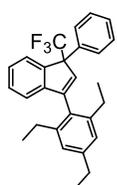
1-(4-Bromophenyl)-3-(2,5-diisopropylphenyl)-1-(trifluoromethyl)-1H-indene (2n) was prepared according to modified general procedure C from 4-(4-bromophenyl)-1,1,1-trifluoro-2,4-diphenylbut-3-yn-2-ol (102 mg, 0.288 mmol) and diisopropylbenzene (164 μ L, 0.87 mmol, 3.0 equiv) with 4.7 mg (0.029 mmol) of FeCl_3 , in 1.15 mL of HFIP. The reaction mixture was heated at 80 $^\circ\text{C}$ for 1 h.

Purification by flash column chromatography over silica (with petroleum ether) gave 111 mg (77% yield) of yellow solid. $R_f = 0.88$ (petroleum ether/EtOAc 9:1). ^1H NMR (500 MHz, CDCl_3): δ (ppm) 7.57–7.29 (m, 8H), 7.22–7.12 (m, 3H), 6.11 (s, 1H), 2.88 (sept, $J = 6.4$ Hz, 2H), 1.17 (d, $J = 6.8$ Hz, 3H), 1.02 (d, $J = 6.8$ Hz, 3H), 0.99 (d, $J = 6.8$ Hz, 3H), 0.74 (d, $J = 6.8$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ (ppm) 148.5, 143.7, 141.8, 141.1, 141.0, 138.1, 136.4 (q, $J = 1.7$ Hz), 134.8, 131.9, 128.7 (q, $J = 1.7$ Hz), 128.2, 128.1, 127.9, 127.8, 126.8 (q, $J = 281.8$ Hz), 126.7, 126.1, 125.7, 121.5, 64.4 (q, $J = 26.4$ Hz), 29.4, 27.1, 24.3, 23.9, 23.6, 23.4z. ^{19}F NMR (376.5 MHz, CDCl_3 , CF_3COOH -ext. st.): δ (ppm) –64.5 (s, 3F). HRMS (APPI $^+$ -Orbitrap): m/z for $\text{C}_{28}\text{H}_{26}^{81}\text{BrF}_3$ $[\text{M}]^+$: calculated 500.1150; found 500.1145 (–1.0 ppm).



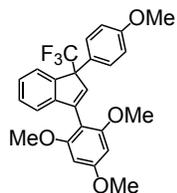
3-(4-(1-Chloro-3,5-dimethylphenyl))-1-phenyl-1-(trifluoro-methyl)-1H-indene (2s) was prepared according to a modification of general procedure B from 1,1,1-trifluoro-2,4-diphenylbut-3-yn-2-ol (113 mg, 0.410 mmol) and 5-chloro-*m*-xylene (165 μ L, 1.23 mmol, 3.0 equiv) with 6.1 mg (0.041 mmol) of FeCl_3 , in 1.6 mL of HFIP. The reaction mixture was heated at 80 $^\circ\text{C}$ for 24 h. Purification by flash column chromatography over

silica (petroleum ether) gave 31 mg (19 % yield) of a white solid. $R_f = 0.31$ (petroleum ether). ^1H NMR (500 MHz, CDCl_3): δ (ppm): 7.64 (d, $J = 6.8$ Hz, 1H), 7.55 (d, $J = 6.8$ Hz, 2H), 7.37–7.27 (m, 5H), 7.16 (s, 1H), 6.98 (s, 1H), 6.95–6.91 (m, 1H), 6.51 (s, 1H), 2.33 (s, 3H), 2.05 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ (ppm) 144.7, 144.4, 143.2, 139.3, 138.6, 134.8, 134.6, 133.8, 129.7, 129.3, 128.9, 128.8, 128.2, 127.8, 127.7, 126.7, 126.7 (q, $J = 281.1$ Hz), 125.5, 121.4, 65.0 (q, $J = 26.8$ Hz), 21.1, 20.6. ^{19}F NMR (282 MHz, CDCl_3 , CF_3COOH -ext. st.): δ (ppm) –67.7 (s, 3F). HRMS (APPI $^+$ -Orbitrap) m/z : $[\text{M}]^+$ calculated for $\text{C}_{24}\text{H}_{18}^{35}\text{ClF}_3$ 398.1044; found 398.1050 (1.5 ppm).



1-Phenyl-3-(2,4,6-triethylphenyl)-1-(trifluoromethyl)-1H-indene (2x) was prepared according to general procedure C from 1,1,1-trifluoro-2,4-diphenylbut-3-yn-2-ol (117 mg, 0.424 mmol) and 1,3,5-triethylbenzene (239 μ L, 1.27 mmol, 3.0 equiv) with 6.9 mg (0.042 mmol) of FeCl_3 , in 1.69 mL of HFIP. The reaction mixture was heated at 80 $^\circ\text{C}$ for 24 h. Purification by flash column chromatography over silica (petroleum ether) gave 127 mg (71% yield) of colorless oil. $R_f = 0.88$ (petroleum ether/EtOAc 9:1). ^1H NMR (500 MHz, CDCl_3) δ (ppm) 7.67–7.62 (m, 1H), 7.57 (d, $J = 6.9$ Hz, 2H), 7.36–7.29 (m, 5H), 7.03 (s, 1H), 7.00 (s, 1H), 6.96–6.91 (m, 1H), 6.48 (s, 1H), 2.69 (q, $J = 7.6$ Hz, 2H), 2.57–2.27 (m, 4H), 1.30 (t, $J = 7.6$ Hz, 3H), 1.09 (t, $J = 7.5$ Hz, 3H), 0.98 (t, $J = 7.5$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3) δ (ppm) 146.4, 146.1, 144.3, 143.3, 143.3, 142.9, 134.9, 133.9, 129.4, 128.9, 128.8, 128.1, 127.8, 126.9 (q, $J = 282.5$ Hz), 126.7, 125.7, 125.5, 125.3, 121.6, 64.8 (q, $J = 26.7$ Hz), 28.9, 27.0, 26.9, 16.3, 16.2, 15.6. ^{19}F NMR (282 MHz, CDCl_3 , CF_3COOH -ext. st.): δ (ppm) –67.9

(s, 3F). HRMS (APPI⁺-Orbitrap) *m/z*: [M]⁺. Calcd for C₂₈H₂₇F₃ 420.2059; Found 420.2055 (−1.2 ppm).

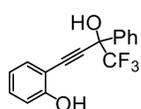


3-(2,4,6-Trimethoxyphenyl)-1-(4-methoxyphenyl)-1-(trifluoromethyl)-1H-indene (**2y**) was prepared according to a modification of general procedure C from 1,1,1-trifluoro-2-(4-methoxyphenyl)-4-phenylbut-3-yn-2-ol (258 mg, 0.841 mmol) and 1,3,5-trimethoxybenzene (424 mg, 2.52 mmol, 3.0 equiv) with 13.6 mg (0.084 mmol) of FeCl₃, in 3.4 mL of HFIP. The reaction mixture was heated at 120 °C

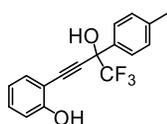
for 24 h in a high-pressure reaction tube. Purification by flash column chromatography over silica (petroleum ether/EtOAc 40:1 to 30:1) gave 364 mg (95% yield) of a yellow solid. *R*_f = 0.21 (petroleum ether/EtOAc 9:1). ¹H NMR (500 MHz, CDCl₃) δ (ppm) 7.64–7.58 (m, 3H), 7.30 (td, *J* = 1.0, 7.5 Hz, 1H), 7.26 – 7.22 (m, 1H), 7.04 (d, *J* = 7.5 Hz, 1H), 6.91 – 6.84 (m, 2H), 6.58 (s, 1H), 6.26 (s, 2H), 3.89 (s, 3H), 3.79 (s, 3H), 3.76–3.70 (m, 6H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ (ppm) 161.5, 159.4, 159.3, 159.1, 145.4, 143.5, 139.8, 135.3 (q, *J* = 1.8 Hz), 129.1 (q, *J* = 1.8 Hz), 128.2, 127.4, 127.0 (q, *J* = 282.4 Hz), 125.8, 124.7, 121.9, 113.9, 104.8, 91.2, 91.1, 63.9 (q, *J* = 26.8 Hz), 56.2, 55.9, 55.5, 55.3. ¹⁹F NMR (282 MHz, CDCl₃, CF₃COOH-ext. st.): δ (ppm) – 66.7 (s, 3F). HRMS (ESI-Orbitrap) *m/z*: [M+H]⁺ Calcd for C₂₆H₂₄F₃O₄ 457.1621; Found 457.1611 (−2.2 ppm).

Preparation of tertiary propargylic alcohols for synthesis of chromenes

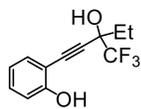
General procedure D:³³ **Step 1.** To a 0.5 M solution of ethynyl magnesium bromide (10 mmol) in THF was slowly added aryl trifluoromethyl ketone (10 mmol) in THF (20 mL). After 3 h at ambient temperature the reaction mixture was quenched first with water and then with saturated NH₄Cl(aq). The aqueous layer was extracted with Et₂O. The combined organic layers were dried over Na₂SO₄, filtered and concentrated under reduced pressure to afford colored oil (2-aryl-1,1,1-trifluoro-3-butyne-2-ol - compound **A**) that was engaged in the next step without further purification. **Step 2.** To a solution of 2-iodophenol (10 mmol) and imidazole (20 mmol) in dry THF (20 mL) was added *tert*-butyldimethylsilyl chloride (20 mmol) in one portion and the reaction mixture was stirred at ambient temperature for 1 h. The mixture was then diluted with CH₂Cl₂ and filtered through celite. The residue was purified by flash column chromatography (petroleum ether) to provide the desired product (1-iodo-2-(*tert*-butyldimethylsilyloxy)benzene - compound **B**). **Step 3.** To a stirred solution of compound **B** (10 mmol) in Et₃N (20 mL) under argon were sequentially added Pd(PPh₃)₂Cl₂ (1 mol %) and CuI (2 mol %) at ambient temperature. Then compound **A** (1.3 equiv) was added and the mixture was stirred overnight. The reaction was quenched with saturated NH₄Cl (aq), extracted with Et₂O, dried over Na₂SO₄, and was purified by flash column chromatography (petroleum ether/EtOAc 9:1). To the isolated product (10 mmol) in THF (20 mL) was added tetra-*n*-butyl ammonium fluoride (1.2 equiv) at room temperature for 30 min. The reaction was quenched by adding water and extracted with EtOAc, dried over Na₂SO₄. The crude material was purified by column chromatography (petroleum ether/EtOAc 10:1) to give the pure propargylic alcohol that was used for subsequent synthesis of chromenes.



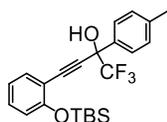
2-(4,4,4-Trifluoro-3-hydroxy-3-phenylbut-1-yn-1-yl)phenol was prepared according to general procedure D using 2,2,2-trifluoro-1-phenylethan-1-one (1.4 mL, 10 mmol). Purification by flash column chromatography over silica (petroleum ether/EtOAc 9:1) gave 263 mg (90% yield) of light yellow solid. Mp: 92–93 °C. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.85–7.76 (m, 2H), 7.47–7.44 (m, 3H), 7.42 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.33 (ddd, *J* = 8.2, 7.5, 1.5 Hz, 1H), 6.98 (dd, *J* = 7.6, 0.7 Hz, 1H), 6.92 (td, *J* = 7.6, 1.1 Hz, 1H), 5.57 (s, 1H), 3.16 (s, 1H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ (ppm) 157.4, 135.0, 132.5, 132.0, 129.9, 128.6, 127.2, 123.4 (q, *J* = 285.6 Hz), 120.8, 115.5, 107.4, 91.6, 82.9, 73.7 (q, *J* = 32.8 Hz). ¹⁹F NMR (376.5 MHz, CDCl₃, CF₃CO₂H - ext. st.): δ (ppm) –81.1 (s, 3F). HRMS (APPI⁺-Orbitrap) *m/z*: [M+H]⁺ Calcd for C₁₆H₁₂O₂F₃ 293.0784; Found 293.0783 (–0.2 ppm).



2-(4,4,4-Trifluoro-3-hydroxy-3-(*p*-tolyl)but-1-yn-1-yl)phenol was prepared according to general procedure D using 2,2,2-trifluoro-1-(*p*-tolyl)ethan-1-one (1.5 mL, 10 mmol). Purification by flash column chromatography over silica (petroleum ether/EtOAc 9:1) gave 110 mg (36% yield) of brown oil. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.68 (d, *J* = 8.2 Hz, 2H), 7.41 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.36–7.30 (m, 1H), 7.22–7.25 (m, 2H), 6.97 (d, *J* = 8.3 Hz, 1H), 6.92 (t, *J* = 7.6 Hz, 1H), 5.61 (s, 1H), 3.19 (s, 1H), 2.40 (s, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ (ppm) 157.4, 140.0, 132.4, 132.2, 131.9, 129.3, 127.1, 123.5 (q, *J* = 285.8 Hz), 120.8, 115.5, 107.5, 91.8, 82.7, 73.6 (q, *J* = 31.6 Hz), 21.3. ¹⁹F NMR (376.5 MHz, CDCl₃, CF₃CO₂H - ext. st.): δ (ppm) –81.1 (s, 3F). HRMS (APPI⁺-Orbitrap) *m/z*: [M]⁺ Calcd for C₁₇H₁₃O₂F₃ 306.0862; Found 305.0862 (–0.1 ppm).

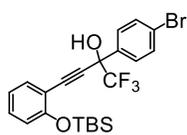


2-(3-Hydroxy-3-(trifluoromethyl)pent-1-yn-1-yl)phenol was prepared according to general procedure D using 1,1,1-trifluorobutan-2-one (1 g, 8 mmol). Purification by flash column chromatography over silica (petroleum ether/EtOAc 9:1) gave 54 mg (22% yield, 70% purity (remainder is 1,1,1-trifluorobutan-2-one) of brown oil. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.36 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.33 (ddd, *J* = 8.2, 7.5, 1.5 Hz, 1H), 6.96 (d, *J* = 8.3 Hz, 2H), 6.90 (td, *J* = 7.6, 1.0 Hz, 1H), 5.57 (s, 1H), 2.70 (s, 1H), 1.98 (q, *J* = 7.6 Hz, 2H), 1.22 (t, *J* = 7.4 Hz, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ (ppm) 157.0, 132.4, 131.7, 124.3 (q, *J* = 285.2 Hz), 120.7, 115.4, 107.6, 90.4, 82.2, 73.2 (q, *J* = 31.1 Hz), 28.4, 7.9. ¹⁹F NMR (376.5 MHz, CDCl₃, CF₃CO₂H - ext. st.): δ (ppm) –82.1 (s, 3F). HRMS (APPI⁺-Orbitrap) [M]⁺ Calcd *m/z*: for C₁₂H₁₁O₂F₃ 244.0711; Found 244.0705 (–2.5 ppm).



4-(2-((*Tert*-butyl)dimethylsilyloxy)phenyl)-1,1,1-trifluoro-2-(*p*-tolyl)but-3-yn-2-ol was prepared according to general procedure D using 2,2,2-trifluoro-1-(*p*-tolyl)ethan-1-one (1.5 mL, 10 mmol), without deprotection step. Purification by flash column chromatography over silica (petroleum ether/EtOAc 9:1) gave 362 mg (86% yield) of brown oil. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.69 (d, *J* = 8.1 Hz, 2H), 7.45 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.28–7.19 (m, 3H), 6.93 (t, *J* = 7.5 Hz, 1H), 6.84 (d, *J* = 8.3 Hz, 1H), 3.02 (s, 1H), 2.38 (s, 3H), 0.97 (s, 9H), 0.24 (s, 3H), 0.23 (s, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ (ppm) 156.9, 139.3, 134.3, 132.5, 130.7, 128.9, 127.2, 123.1 (q, *J* = 285.3 Hz), 121.1, 119.2, 113.4, 87.8, 85.5, 73.3 (q, *J* = 31.9 Hz), 25.6, 21.3, 18.3, –4.2. ¹⁹F NMR (376.5 MHz,

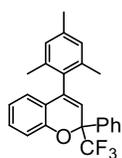
CDCl₃, CF₃CO₂H - ext. st.): δ (ppm) -78.9 (s, 3F). HRMS (APPI⁺-Orbitrap) m/z : [M+H]⁺ calculated for C₂₃H₂₈O₂F₃Si 421.1805; Found 421.1797 (-2.0 ppm).



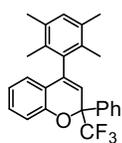
2-(4-Bromophenyl)-4-(2-((tert-butyl)dimethylsilyloxy)phenyl)-1,1,1-trifluorobut-3-yn-2-ol was prepared according to general procedure D using 1-(4-bromophenyl)-2,2,2-trifluoroethan-1-one (2.5 g, 10 mmol), without deprotection step. Purification by flash column chromatography over silica (petroleum ether/EtOAc 9:1) gave 427 mg (88% yield) of brown oil. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.68 (d, J = 8.6 Hz, 2H), 7.54 (d, J = 8.6 Hz, 2H), 7.44 (dd, J = 7.7, 1.7 Hz, 1H), 7.28–7.25 (m, 1H), 6.93 (td, J = 7.6, 1.0 Hz, 1H), 6.84 (d, J = 8.3 Hz, 1H), 3.09 (s, 1H), 0.95 (s, 9H), 0.23 (s, 3H), 0.22 (s, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ (ppm) 157.0, 134.9, 134.6, 131.7, 131.2, 129.4, 124.1, 123.4 (q, J = 286.4 Hz), 121.4, 119.8, 113.4, 87.4, 86.4, 73.4 (q, J = 32.8 Hz), 25.8, 18.5, -3.9. ¹⁹F NMR (376.5 MHz, CDCl₃, CF₃CO₂H - ext. st.): δ (ppm) -81.0 (s, 3F). HRMS (APPI⁺-Orbitrap) m/z [M]⁺ Calcd for C₂₂H₂₅O₂⁷⁹BrF₃Si 485.0754; Found 485.0756 (0.4 ppm).

General procedure E for synthesis of CF₃-chromenes and CF₃-alkenes. To a solution of propargylic alcohol (0.25 mmol) in HFIP (125 μ L), aryl nucleophile was added (0.75 mmol) and TfOH (2.2 μ L, 10 mol%). The reaction was stirred at 50 °C for 16 h. The crude reaction mixture was directly transferred for silica gel chromatography.

Characterization data for chromenes.

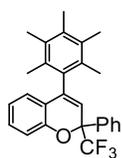


4-Mesityl-2-phenyl-2-(trifluoromethyl)-2H-chromene (**4a**) was prepared according to general procedure E from 2-(4,4,4-trifluoro-3-hydroxy-3-phenylbut-1-yn-1-yl)phenol (73 mg, 0.25 mmol) and mesitylene (105 μ L, 0.750 mmol), with 2.2 μ L (0.025 mmol) of triflic acid, in 0.125 mL of HFIP (16 h, 50 °C). Purification by flash column chromatography over silica (petroleum ether) gave 101 mg (quantitative yield) of white solid. Mp: 90–92 °C. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.67 (d, J = 7.5 Hz, 2H), 7.41–7.33 (m, 3H), 7.20 (t, J = 7.7 Hz, 1H), 7.11 (d, J = 8.1 Hz, 1H), 6.94 (d, J = 10.0 Hz, 2H), 6.77 (t, J = 7.5 Hz, 1H), 6.54 (d, J = 7.6 Hz, 1H), 6.01 (s, 1H), 2.33 (s, 3H), 2.13 (s, 3H), 2.00 (s, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ (ppm) 151.7, 137.9, 137.5, 136.9, 133.2, 130.6, 129.3, 128.7, 128.6, 128.5, 127.1, 125.7, 125.0 (q, J = 284.6 Hz), 122.5, 120.9, 118.3, 116.9, 80.4 (q, J = 30.1 Hz), 21.4, 20.1, 19.9. ¹⁹F NMR (376.5 MHz, CDCl₃, CF₃CO₂H, - ext. st.): δ (ppm) -80.3 (s, 3F). HRMS (APPI⁺-Orbitrap) m/z : [M-H]⁺ for C₂₅H₂₀OF₃ Calcd 393.1461; Found 393.1460 (-0.1 ppm).

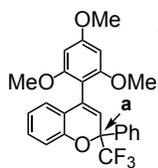


2-Phenyl-4-(2,3,5,6-tetramethylphenyl)-2-(trifluoromethyl)-2H-chromene (**4b**) was prepared according to general procedure E from 2-(4,4,4-trifluoro-3-hydroxy-3-phenylbut-1-yn-1-yl)phenol (73 mg, 0.25 mmol) and durene (102 mg, 0.75 mmol), with 2.2 μ L (0.025 mmol) of triflic acid, in 0.125 mL of HFIP (16 h, 50 °C). Purification by flash column chromatography over silica (petroleum ether) gave 88 mg (86% yield) of white solid. Mp: 158–160 °C. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.66 (d, J = 7.3 Hz, 2H), 7.42–7.33 (m, 3H), 7.22–7.18 (m, 1H), 7.12 (dd, J = 8.1, 0.9 Hz, 1H), 7.01 (s, 1H),

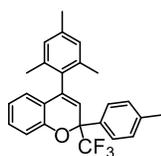
6.77 (td, $J = 7.5, 1.1$ Hz, 1H), 6.53 (dd, $J = 7.6, 1.4$ Hz, 1H), 5.99 (s, 1H), 2.26 (s, 3H), 2.24 (s, 3H), 2.05 (s, 3H), 1.89 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ (ppm) 151.6, 139.0, 137.5, 136.2, 134.3, 134.1, 132.8, 132.6, 131.5, 130.5, 129.3, 128.6, 127.2, 126.0, 124.3 (q, $J = 284.6$ Hz), 122.4, 121.3, 118.0, 116.8, 80.4 (q, $J = 30.5$ Hz), 20.4, 20.3, 16.8, 16.6. ^{19}F NMR (376.5 MHz, CDCl_3 , $\text{CF}_3\text{CO}_2\text{H}$ - ext. st.): δ (ppm) -80.3 (s, 3F). HRMS (APPI⁺-Obitrap) m/z : $[\text{M}]^+$. Calcd for $\text{C}_{26}\text{H}_{23}\text{OF}_3$ 408.1696; Found 408.1698 (0.6 ppm).



4-(2,3,4,5,6-Pentamethylphenyl)-2-phenyl-2-(trifluoromethyl)-2H-chromene (4c) was prepared according to general procedure E from 2-(4,4,4-trifluoro-3-hydroxy-3-phenylbut-1-yn-1-yl)phenol (72.5 mg, 0.25 mmol) and pentamethyl-benzene (111 mg, 0.75 mmol), with 2.2 μL (0.025 mmol) of triflic acid, in 0.125 mL of HFIP (16 h, 50 $^\circ\text{C}$). Purification by flash column chromatography over silica (petroleum ether) gave 132 mg (quantitative yield) of white solid. Mp: 92–94 $^\circ\text{C}$. ^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.65 (d, $J = 7.3$ Hz, 2H), 7.44–7.30 (m, 3H), 7.23–7.17 (m, 1H), 7.12 (dd, $J = 8.1, 1.0$ Hz, 1H), 6.77 (td, $J = 7.5, 1.2$ Hz, 1H), 6.56 (dd, $J = 7.6, 1.5$ Hz, 1H), 6.00 (s, 1H), 2.30 (s, 3H), 2.25 (s, 3H), 2.23 (s, 3H), 2.11 (s, 3H), 1.95 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ (ppm) 151.6, 139.6, 137.5, 136.1, 133.8, 133.2, 132.9, 132.4, 132.2, 130.5, 129.3, 128.6, 127.2, 126.2, 124.4 (q, $J = 284.6$ Hz), 122.4, 121.6, 118.1, 116.8, 80.5 (q, $J = 30.5$ Hz), 18.1, 17.8, 17.2, 16.9, 16.8. ^{19}F NMR (376.5 MHz, CDCl_3 , $\text{CF}_3\text{CO}_2\text{H}$ - ext. st.): δ (ppm) -80.2 (s, 3F). HRMS (APPI⁺-Orbitrap) m/z : $[\text{M}]^+$. Calcd for $\text{C}_{27}\text{H}_{25}\text{OF}_3$ 422.1852; Found 422.1855 (0.7 ppm).

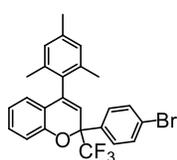


2-Phenyl-2-(trifluoromethyl)-4-(2,4,6-trimethoxyphenyl)-2H-chromene (4d) was prepared according to general procedure E from 2-(4,4,4-trifluoro-3-hydroxy-3-phenylbut-1-yn-1-yl)phenol (73 mg, 0.25 mmol) and 1,3,5-trimethoxybenzene (116 mg, 0.75 mmol), with 2.2 μL (0.025 mmol) of triflic acid, in 0.125 mL of HFIP (16 h, 50 $^\circ\text{C}$). Purification by flash column chromatography over silica (petroleum ether/EtOAc 97:3) gave 47 mg (43% yield) of white solid. Mp: 133–135 $^\circ\text{C}$. ^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.74 (d, $J = 7.4$ Hz, 2H), 7.38–7.32 (m, 3H), 7.11 (t, $J = 6.9$ Hz, 1H), 7.02 (d, $J = 8.1$ Hz, 1H), 6.75 (t, $J = 7.5$ Hz, 1H), 6.64 (d, $J = 7.6$ Hz, 1H), 6.20 (d, $J = 3.4$ Hz, 1H), 6.20 (d, $J = 7.6$ Hz, 1H), 6.13 (s, 1H), 3.87 (s, 3H), 3.69 (s, 3H), 3.67 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ (ppm) 161.8, 159.6, 159.4, 151.4, 137.6, 131.7, 129.6, 129.2, 128.2, 127.9, 125.8, 124.7 (q, $J = 283.8$ Hz), 122.4, 122.0, 120.5, 116.8, 107.3, 91.3, 91.2, 56.3, 56.1, 55.7 (quaternary carbon **a** displayed a very weak signal). ^{19}F NMR (376.5 MHz, CDCl_3 , $\text{CF}_3\text{CO}_2\text{H}$ - ext. st.): δ (ppm) -79.9 (s, 3F). HRMS (APPI⁺-Orbitrap) m/z : $[\text{M}+\text{H}]^+$. Calcd for $\text{C}_{25}\text{H}_{22}\text{O}_4\text{F}_3$ 443.1465; Found 443.1464 (-0.2 ppm).

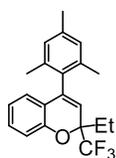


4-Mesityl-2-(p-tolyl)-2-(trifluoromethyl)-2H-chromene (4e) was prepared according to general procedure E from 2-(4,4,4-trifluoro-3-hydroxy-3-(p-tolyl)but-1-yn-1-yl)phenol (77 mg, 0.25 mmol) and mesitylene (105 μL , 0.75 mmol), with 2.2 μL (0.025 mmol) of triflic acid, in 0.125 mL of HFIP (16 h, 50 $^\circ\text{C}$). Purification by flash column chromatography over silica (petroleum ether) gave 55 mg (54% yield) of white solid. **4e** was also prepared according to general procedure E from 4-(2-((tert-

butyldimethylsilyloxy)phenyl)-1,1,1-trifluoro-2-(*p*-tolyl)but-3-yn-2-ol (105 mg, 0.25 mmol) and mesitylene (105 μ L, 0.75 mmol), with 2.2 μ L (0.025 mmol) of triflic acid, in 0.125 mL of HFIP (16 h, 50 $^{\circ}$ C). Purification by flash column chromatography over silica (petroleum ether) gave 290 mg (71% yield) of white solid. Mp: 110–113 $^{\circ}$ C. ^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.55 (d, J = 8.1 Hz, 2H), 7.21–7.17 (m, 3H), 7.09 (dd, J = 8.1, 1.0 Hz, 1H), 6.95 (s, 1H), 6.93 (s, 1H), 6.76 (td, J = 7.5, 1.2 Hz, 1H), 6.54 (dd, J = 7.6, 1.5 Hz, 1H), 6.00 (s, 1H), 2.34 (s, 3H), 2.33 (s, 3H), 2.12 (s, 3H), 2.02 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ (ppm) 151.7, 139.2, 137.8, 137.7, 136.9, 134.5, 133.3, 130.5, 129.3, 128.7, 128.4, 127.1, 125.6, 124.2 (q, J = 284.6 Hz), 122.4, 121.0, 118.5, 116.9, 80.4 (q, J = 30.5 Hz), 24.5, 21.4, 20.1, 19.9. ^{19}F NMR (376.5 MHz, CDCl_3 , $\text{CF}_3\text{CO}_2\text{H}$ - ext. st.): δ (ppm) –80.5 (s, 3F). HRMS (APPI $^+$ -Orbitrap) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{26}\text{H}_{23}\text{OF}_3$ 408.1698; Found 408.1696 (–0.7 ppm).



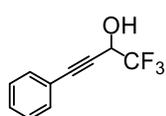
2-(4-Bromophenyl)-4-mesityl-2-(trifluoromethyl)-2H-chromene (**4f**) was prepared according to general procedure E from 2-(4-bromophenyl)-4-(2-((*tert*-butyldimethylsilyloxy)phenyl)-1,1,1-trifluoro-but-3-yn-2-ol (121 mg, 0.25 mmol) and mesitylene (105 μ L, 0.75 mmol), with 2.2 μ L (0.025 mmol) of triflic acid, in 0.125 mL of HFIP (16 h, 50 $^{\circ}$ C). Purification by flash column chromatography over silica (petroleum ether) gave 89 mg (75% yield) white solid. Mp: 113–115 $^{\circ}$ C. ^1H NMR (400 MHz, CDCl_3) δ 7.53 (s, 4H), 7.23–7.18 (m, 1H), 7.09 (d, J = 7.9 Hz, 1H), 6.94 (d, J = 6.9 Hz, 2H), 6.79 (t, J = 7.4 Hz, 1H), 6.55 (dd, J = 1.2, 7.7 Hz, 1H), 5.97 (s, 1H), 2.33 (s, 3H), 2.11 (s, 3H), 2.00 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ (ppm) 151.4, 138.4, 138.0, 136.8, 136.7, 136.5, 133.0, 131.9, 130.8, 128.9, 128.7, 128.5, 125.8, 124.1 (q, J = 284.6 Hz), 123.8, 122.7, 120.8, 117.7, 116.9, 80.1 (q, J = 30.5 Hz), 21.4, 20.1, 19.9. ^{19}F NMR (376.5 MHz, CDCl_3 , $\text{CF}_3\text{CO}_2\text{H}$ - ext. st.): δ (ppm) –80.5 (s, 3F). HRMS (APPI $^+$ -Orbitrap) m/z $[\text{M}]^+$ Calcd for $\text{C}_{25}\text{H}_{21}\text{OBrF}_3$ 473.0722; Found 473.0716 (–1.3 ppm).



2-Ethyl-4-mesityl-2-(trifluoromethyl)-2H-chromene (**4g**) was prepared according to general procedure E from 2-(3-hydroxy-3-(trifluoromethyl)pent-1-yn-1-yl)phenol (61 mg, 0.25 mmol) and mesitylene (105 μ L, 0.75 mmol), with 2.2 μ L (0.025 mmol) of triflic acid, in 0.125 mL of HFIP (16 h, 50 $^{\circ}$ C). Purification by flash column chromatography over silica (petroleum ether) gave 67 mg (77% yield) of colorless oil. ^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.14 (td, J = 8.0, 1.6 Hz, 1H), 6.94 (s, 1H), 6.92 (s, 1H), 6.90 (dd, J = 8.1, 0.8 Hz, 1H), 6.73 (td, J = 7.5, 1.1 Hz, 1H), 6.52 (dd, J = 7.6, 1.6 Hz, 1H), 5.26 (s, 1H), 2.33 (s, 3H), 2.17–2.07 (m, 1H), 2.14 (s, 3H), 2.09 (s, 3H), 1.83 (dq, J = 14.2, 7.3 Hz, 1H), 1.11 (t, J = 7.4 Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ (ppm) 153.4, 139.7, 137.7, 137.1, 136.3, 133.5, 130.4, 128.7, 128.4, 125.5, 125.0 (q, J = 284.6 Hz), 121.8, 119.8, 117.4, 115.8, 80.7 (q, J = 30.5 Hz), 27.9, 21.4, 20.2, 19.8, 7.8. ^{19}F NMR (376.5 MHz, CDCl_3 , $\text{CF}_3\text{CO}_2\text{H}$ - ext. st.): δ (ppm) –83.0 (s, 3F). HRMS (APPI $^+$ -Orbitrap) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{21}\text{H}_{21}\text{OF}_3$ 346.1539; Found 346.1538 (–0.3 ppm).

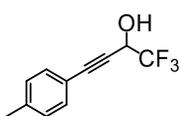
General procedure F for preparation of secondary propargylic alcohols. Secondary propargylic alcohols were prepared via two-step Kitazume/Sato sequence.³⁴ To a mixture of alkyne

(10 mmol) and anhydrous THF (30 mL) at $-78\text{ }^{\circ}\text{C}$ was added *n*-BuLi (10 mmol, 2.5 M solution) for 5 min. After 20 min stirring at $-78\text{ }^{\circ}\text{C}$, ethyl fluoroacetate (10 mmol), boron trifluoride diethyl etherate (12 mmol), and anhydrous THF (20 mL) were added. After an additional 2 h of stirring, the reaction was quenched with brine, extracted with ethyl acetate, and dried over Na_2SO_4 . The resulting ketone was purified by flash chromatography (petroleum ether/EtOAc 9:1). The ketone was dissolved in methanol (10 mL). To the solution was added NaBH_4 (10 mmol) slowly and the reaction solution was stirred for 30 min at room temperature. The mixture was quenched by adding brine and extracted with ethyl acetate, dried over Na_2SO_4 . Finally, purification by flash chromatography yielded the secondary propargylic alcohols.



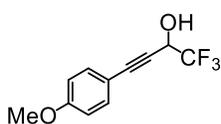
1,1,1-Trifluoro-4-phenylbut-3-yn-2-ol was prepared according to general procedure F using phenylacetylene (0.54 mL, 5.0 mmol). Purification by flash column chromatography over silica (petroleum ether/EtOAc 9:1) gave 88 mg (44% yield) of yellow oil. The experimental data are in agreement with the literature.³⁵

^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.50–7.48 (m, 2H), 7.42–7.32 (m, 3H), 4.94–4.88 (m, 1H), 2.52 (d, $J = 8.3$ Hz, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ (ppm) 132.4, 129.9, 128.8, 123.2 (q, $J = 281.9$ Hz), 121.2, 88.4, 80.7, 63.3 (q, $J = 36.5$ Hz). ^{19}F NMR (376.5 MHz, CDCl_3 , $\text{CF}_3\text{CO}_2\text{H}$ - ext. st.): δ (ppm) -80.2 (s, 3F).



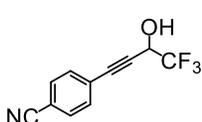
1,1,1-Trifluoro-4-(p-tolyl)but-3-yn-2-ol was prepared according to general procedure F using 1-ethynyl-4-methylbenzene (0.63 mL, 5.0 mmol). Purification by flash column chromatography over silica (petroleum ether/EtOAc 9:1) gave 98 mg (46% yield) of white solid. Mp: $69\text{--}71\text{ }^{\circ}\text{C}$.

^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.40 (d, $J = 8.0$ Hz, 2H), 7.17 (d, $J = 7.9$ Hz, 2H), 4.95–4.89 (m, 1H), 2.47 (d, $J = 6.7$ Hz, 1H), 2.39 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ (ppm) 140.2, 132.3, 129.5, 123.1 (q, $J = 281.7$ Hz), 118.1, 88.6, 80.1, 63.3 (q, $J = 36.4$ Hz), 21.6. ^{19}F NMR (376.5 MHz, CDCl_3 , $\text{CF}_3\text{CO}_2\text{H}$ - ext. st.): δ (ppm) -80.3 (s, 3F). HRMS (APPI⁺-Orbitrap) m/z : for $\text{C}_{11}\text{H}_{10}\text{OF}_3$ [$\text{M}+\text{H}$]⁺. Calcd 215.0678; found 215.0678 (-0.0 ppm).



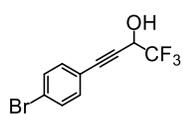
1,1,1-Trifluoro-4-(4-methoxyphenyl)but-3-yn-2-ol was prepared according to general procedure F using 1-ethynyl-4-methoxybenzene (0.65 mL, 5.0 mmol). Purification by flash column chromatography over silica (petroleum ether/EtOAc 85:15) gave 69 mg (30% yield) of yellow oil.

^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.44–7.39 (m, 2H), 6.89–6.83 (m, 2H), 4.89 (dq, $J = 5.7, 8.2$ Hz, 1H), 3.82 (s, 3H), 2.47 (d, $J = 8.3$ Hz, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ (ppm) 160.8, 133.9, 123.3 (q, $J = 282.0$ Hz), 114.4, 113.2, 88.4, 79.5, 63.3 (q, $J = 36.7$ Hz), 55.7. ^{19}F NMR (376.5 MHz, CDCl_3 , $\text{CF}_3\text{CO}_2\text{H}$ - ext. st.): δ (ppm) -78.3 (s, 3F). HRMS (APPI⁺): m/z for $\text{C}_{11}\text{H}_9\text{O}_2\text{F}_3$ ($[\text{M}]^+$): calculated 230.0555; found 230.0551 (-1.7 ppm).



4-(4,4,4-Trifluoro-3-hydroxybut-1-yn-1-yl)benzonitrile was prepared according to general procedure F using 1-ethynyl-4-isocyanobenzene (0.64 g, 5.0 mmol). Purification by flash column chromatography over silica (petroleum ether/EtOAc 9:1) gave 56 mg (25% yield) of yellow solid. Mp: $90\text{--}92\text{ }^{\circ}\text{C}$. ^1H

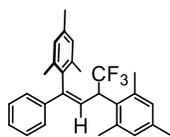
NMR (400 MHz, CDCl₃): δ (ppm) 7.65 (d, J = 8.1 Hz, 2H), 7.58 (d, J = 8.4 Hz, 2H), 4.98-4.91 (m, 1H), 2.59 (d, J = 8.4 Hz, 1H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 132.7, 132.3, 125.8, 122.7 (q, J = 282.0 Hz), 118.2, 113.1, 86.1, 84.6, 63.1 (q, J = 36.8 Hz). ¹⁹F NMR (376.5 MHz, CDCl₃, CF₃CO₂H - ext. st.): δ (ppm) -80.0 (s, 3F). HRMS (APPI⁺-Orbitrap) m/z : [M+H]⁺ Calcd for C₁₁H₇ONF₃ 226.0480; Found 226.0475 (-2.3 ppm).



4-(4-Bromophenyl)-1,1,1-trifluorobut-3-yn-2-ol was prepared according to general procedure F using 1-ethynyl-4-bromobenzene (0.60 mL, 5.0 mmol). Purification by flash column chromatography over silica (petroleum ether/EtOAc 9:1) gave 167 mg (60% yield) of yellow/dark yellow solid. Mp: 62–63 °C. ¹H

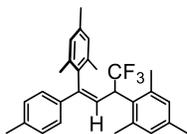
NMR (400 MHz, CDCl₃): δ (ppm) 7.49 (d, J = 8.4 Hz, 2H), 7.34 (d, J = 8.4 Hz, 2H), 4.91–4.88 (m, 1H), 2.50 (d, J = 7.0 Hz, 1H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ (ppm) 133.8, 132.2, 124.4, 123.1 (q, J = 282.4 Hz), 120.1, 87.2, 81.8, 62.3 (q, J = 36.6 Hz). ¹⁹F NMR (376.5 MHz, CDCl₃, CF₃CO₂H - ext. st.): δ (ppm) -80.2 (s, 3F). HRMS (APPI⁺-Orbitrap) m/z : [M]⁺ Calcd for C₁₀H₅O⁷⁹BrF₃ 276.9470; found 276.9473 (0.8 ppm).

Characterization data for Friedel-Crafts reaction products of secondary propargylic alcohols



(*Z*)-2,2'-(4,4,4-Trifluoro-1-phenylbut-1-ene-1,3-diyl)bis(1,3,5-trimethylbenzene) (**6a**) was prepared according to general procedure E from 1,1,1-trifluoro-4-phenylbut-3-yn-2-ol (50 mg, 0.25 mmol) and mesitylene (105 μ L, 0.75 mmol), with 2.2 μ L (0.025 mmol) of triflic acid, in 0.125 mL of HFIP (16 h, 50 °C).

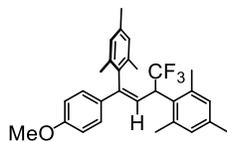
Purification by flash column chromatography over silica (petroleum ether) gave 80 mg (75% yield) of white solid. Mp: 135–136 °C. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.27-7.21 (m, 5H), 6.95 (s, 1H), 6.92 (d, J = 8.7 Hz, 1H), 6.79 (s, 1H), 6.76 (s, 1H), 6.65 (d, J = 5.1 Hz, 1H), 4.38-4.29 (m, 1H), 2.51 (s, 3H), 2.28 (s, 3H), 2.27 (s, 3H), 2.19 (s, 3H), 2.18 (s, 3H), 1.14 (s, 3H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 143.0, 139.2, 138.9, 137.6, 137.6, 137.3, 137.2, 135.3, 134.3, 130.9, 129.2, 128.7, 128.7, 128.6, 128.4, 127.9, 127.6 (q, J = 280.9 Hz) 125.9, 121.7, 45.8 (q, J = 27.8 Hz), 22.7 (q, J = 3.2 Hz), 21.2, 20.9, 19.9, 19.6, 18.4. ¹⁹F NMR (376.5 MHz, CDCl₃, CF₃CO₂H - ext. st.): δ (ppm) -68.4 (s, 3F). HRMS (APPI⁺-Orbitrap) m/z : [M]⁺ Calcd for C₂₈H₂₉F₃ 422.2216; Found 422.2217 (0.4 ppm).



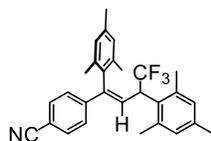
(*Z*)-2,2'-(4,4,4-Trifluoro-1-(*p*-tolyl)but-1-ene-1,3-diyl)bis(1,3,5-trimethylbenzene) (**6b**) was prepared according to general procedure E from 1,1,1-trifluoro-4-(*p*-tolyl)but-3-yn-2-ol (53 mg, 0.25 mmol) and mesitylene (105 μ L, 0.75 mmol), with 2.2 μ L (0.025 mmol) of triflic acid, in 0.125 mL of HFIP (16 h, 50 °C). Purification by flash column chromatography over silica

(petroleum ether) gave 84 mg (77% yield) of white solid. Mp: 90–91 °C. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.16 (d, J = 8.3 Hz, 2H), 7.08 (d, J = 8.2 Hz, 2H), 6.95 (s, 1H), 6.87 (d, J = 8.7 Hz, 1H), 6.76 (s, 1H), 6.65 (d, J = 4.5 Hz, 2H), 4.37–4.27 (m, 1H), 2.50 (s, 3H), 2.31 (s, 3H), 2.28 (s, 3H), 2.20 (s, 3H), 2.17 (s, 3H), 1.39 (s, 3H), 1.13 (s, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 142.8, 139.2, 137.8, 137.6, 137.5, 137.1, 136.0, 135.3, 134.5, 130.9, 129.4 (2C), 129.1, 128.6,

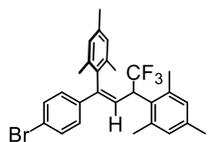
128.4, 127.6 (q, $J = 281.2$ Hz), 125.8 (2C), 120.7, 45.8 (q, $J = 27.8$ Hz), 22.7 (q, $J = 3.1$ Hz), 21.3, 21.2, 20.9, 19.9, 19.6, 18.3. ^{19}F NMR (376.5 MHz, CDCl_3 , $\text{CF}_3\text{CO}_2\text{H}$ - ext. st.): δ (ppm) -68.3 (s, 3F). HRMS (APPI $^+$ -Orbitrap) m/z : $[\text{M}]^+$. Calcd for $\text{C}_{29}\text{H}_{31}\text{F}_3$ 436.2372; Found 436.2377 (1.1 ppm).



(Z)-2,2'-(4,4,4-Trifluoro-1-(4-methoxyphenyl)but-1-ene-1,3-diyl)bis(1,3,5-trimethylbenzene) (**6c**) was prepared according to general procedure E from 1,1,1-trifluoro-4-(4-methoxyphenyl)but-3-yn-2-ol (58 mg, 0.25 mmol) and mesitylene (105 μL , 0.75 mmol), with 2.2 μL (0.025 mmol) of triflic acid, in 0.125 mL of HFIP (16 h, 50 $^\circ\text{C}$). Purification by flash column chromatography over silica (petroleum ether/EtOAc 98:2) gave 91 mg (81% yield) of colorless oil. ^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.22 (d, $J = 8.8$ Hz, 2H), 6.98 (s, 1H), 6.83 (d, $J = 8.5$ Hz, 2H), 6.79 (d, $J = 6.9$ Hz, 2H), 6.68 (d, $J = 5.2$ Hz, 2H), 4.40–4.26 (m, 1H), 3.81 (s, 3H), 2.53 (s, 3H), 2.31 (s, 3H), 2.23 (s, 3H), 2.20 (s, 3H), 1.42 (s, 3H), 1.17 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 159.5, 142.4, 139.2, 137.6, 137.5, 137.1 (q, $J = 2.6$ Hz), 135.2, 134.6, 131.5, 130.9, 129.1, 128.6, 128.4, 127.7 (q, $J = 281.1$ Hz), 127.1 (2C), 119.6, 114.0 (2C), 55.4, 45.8 (q, $J = 27.7$ Hz), 21.2, 20.9, 19.9, 19.6, 18.3. ^{19}F NMR (376.5 MHz, CDCl_3 , $\text{CF}_3\text{CO}_2\text{H}$ - ext. st.): δ (ppm) -67.4 (s, 3F). HRMS (APPI $^+$ -Orbitrap) m/z : $[\text{M}]^+$. Calcd for $\text{C}_{29}\text{H}_{31}\text{OF}_3$ 452.2322; Found 452.2323 (0.3 ppm).

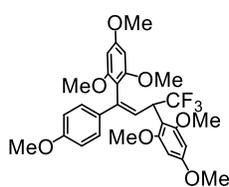


(Z)-4-(4,4,4-Trifluoro-1,3-dimesitylbut-1-en-1-yl)benzotrile (**6d**) was prepared according to general procedure E from 4-(4,4,4-trifluoro-3-hydroxybut-1-yn-1-yl)benzotrile (56 mg, 0.25 mmol) and mesitylene (105 μL , 0.75 mmol), with 2.2 μL (0.025 mmol) of triflic acid, in 0.125 mL of HFIP (88 h, 100 $^\circ\text{C}$). Purification by flash column chromatography over silica (petroleum ether/EtOAc 98:2) gave 25 mg (22% yield) of colorless oil. ^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.56 (d, $J = 8.5$ Hz, 2H), 7.35 (d, $J = 8.5$ Hz, 2H), 7.06 (d, $J = 8.6$ Hz, 1H), 6.98 (s, 1H), 6.77 (s, 1H), 6.67 (d, $J = 8.6$ Hz, 2H), 4.40–4.30 (m, 1H), 2.48 (s, 3H), 2.29 (s, 3H), 2.20 (s, 3H), 2.14 (s, 3H), 1.40 (s, 3H), 1.10 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ (ppm) 143.3, 141.8, 139.3, 138.0, 137.6, 137.5, 137.4, 135.2, 133.0, 132.6, 131.0, 129.3, 128.9, 128.7, 128.0, 127.8 (q, $J = 280.7$ Hz), 126.4, 125.4, 119.0, 111.3, 46.0 (q, $J = 28.0$ Hz), 22.7 (q, $J = 3.8$ Hz), 21.2, 20.9, 19.8, 19.6, 18.3. ^{19}F NMR (376.5 MHz, CDCl_3 , $\text{CF}_3\text{CO}_2\text{H}$ - ext. st.): δ (ppm) -67.3 (s, 3F). HRMS (APPI $^+$ -Orbitrap) m/z : $[\text{M}]^+$. Calcd for $\text{C}_{29}\text{H}_{28}\text{NF}_3$ 447.2168; Found 447.2172 (0.8 ppm).

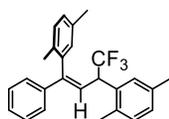


(Z)-2,2'-(1-(4-Bromophenyl)-4,4,4-trifluorobut-1-ene-1,3-diyl)bis(1,3,5-trimethylbenzene) (**6e**) was prepared according to general procedure E from 4-(4-bromophenyl)-1,1,1-trifluorobut-3-yn-2-ol (70 mg, 0.25 mmol) and mesitylene (105 μL , 0.75 mmol), with 2.2 μL (0.025 mmol) of triflic acid, in 0.125 mL of HFIP (16 h, 50 $^\circ\text{C}$). Purification by flash column chromatography over silica (petroleum ether) gave 77 mg (61% yield) of colorless oil. ^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.40 (d, $J = 8.6$ Hz, 2H), 7.13 (d, $J = 8.6$ Hz, 2H), 6.96 (s, 1H), 6.92 (d, $J = 8.7$ Hz, 1H), 6.77 (s, 1H), 6.67 (d, $J = 6.1$ Hz, 2H), 4.37–4.27 (m, 1H), 2.48 (s, 3H), 2.29 (s, 3H), 2.21 (s, 3H), 2.16 (s, 3H), 1.40 (s, 3H), 1.13 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ (ppm) 142.3, 139.4, 138.0, 137.8, 137.7, 137.5, 135.4, 134.5, 133.9, 132.0, 131.1, 129.4, 128.9, 128.7, 123.0 (q, $J = 281.2$ Hz), 127.7, 126.0, 123.1, 122.2, 46.1 (q, $J = 27.8$ Hz), 22.9, 21.5, 21.0, 20.1, 19.8, 18.5. ^{19}F

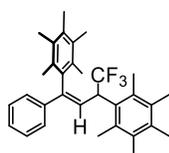
NMR (376.5 MHz, CDCl₃, CF₃CO₂H - ext. st.): δ (ppm) -67.3 (s, 3F). HRMS (APPI⁺-Orbitrap) m/z : [M]⁺. Calcd for C₂₈H₂₈⁷⁹BrF₃ 500.1321; Found 500.1331 (1.9 ppm).



(*Z*)-2,2'-(4,4,4-Trifluoro-1-(4-methoxyphenyl)but-1-ene-1,3-diyl)bis(1,3,5-trimethoxybenzene) (**6f**) was prepared according to general procedure E from 1,1,1-trifluoro-4-(4-methoxyphenyl)but-3-yn-2-ol (58 mg, 0.25 mmol) and 1,3,5-trimethoxybenzene (116 mg, 0.75 mmol), with 2.2 μ L (0.025 mmol) of triflic acid, in 0.125 mL of HFIP (16 h, 50 °C). Purification by flash column chromatography over silica (petroleum ether/EtOAc 8:2) gave 100 mg (73% yield) of white solid. Mp: 128–129 °C. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.24 (d, J = 8.9 Hz, 2H), 6.79 (dd, J = 21.3, 8.5 Hz, 3H), 6.20 (d, J = 2.1 Hz, 1H), 6.08 (s, 1H), 5.90 (s, 1H), 5.87 (d, J = 2.1 Hz, 1H), 4.60–4.49 (m, 1H), 3.82 (s, 6H), 3.78 (s, 3H), 3.76 (s, 6H), 3.43 (s, 3H), 3.07 (s, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ (ppm) 161.1, 160.8, 159.2, 159.0, 158.3, 135.5, 133.9, 127.8 (q, J = 280.9 Hz), 127.3, 123.2, 113.7, 109.5, 105.9, 91.6, 90.5, 90.4, 90.2, 56.4, 56.2, 55.7, 55.6 (2C), 55.5, 55.2, 30.2 (q, J = 27.8 Hz). ¹⁹F NMR (376.5 MHz, CDCl₃, CF₃CO₂H - ext. st.): δ (ppm) -68.2 (s, 3F). HRMS (ESI-Orbitrap) m/z : [M+H]⁺ Calcd for C₂₉H₃₂O₇F₃ 549.2095; Found 549.2114 (3.6 ppm).

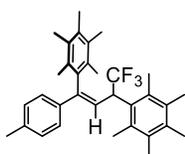


(*Z*)-2,2'-(4,4,4-Trifluoro-1-phenylbut-1-ene-1,3-diyl)bis(1,4-dimethylbenzene) (**6g**) was prepared according to general procedure E from 1,1,1-trifluoro-4-phenylbut-3-yn-2-ol (50 μ L, 0.25 mmol) and *p*-xylene (92 μ L, 0.75 mmol), with 2.2 μ L (0.025 mmol) of triflic acid, in 0.125 mL of HFIP (16 h, 50 °C). Purification by flash column chromatography over silica (petroleum ether) gave 48 mg (49% yield) of colorless oil which was isolated as a 6:4 mixture of stereoisomers as determined by ¹H NMR. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 6.69 (d, J = 9.7 Hz, 1H, major), 6.68 (d, J = 9.7 Hz, 1H, minor), 6.36 (s, 1H, minor), 4.39–4.22 (m, 1H, minor), 4.15–4.01 (m, 1H, major), 2.41 (s, 3H, minor), 2.34 (s, 6H, major), 2.16 (s, 3H, major), 2.06 (s, 3H, major), 1.78 (s, 3H, minor), 1.68 (s, 3H, minor), 1.45 (s, 3H, minor). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 146.1, 145.8, 140.0, 139.8, 138.0, 137.8, 135.7, 135.7, 135.3, 134.5, 134.0, 133.8, 133.7, 133.6, 133.3, 130.5, 130.4, 130.4, 130.3, 130.2, 129.7, 129.2, 128.8, 128.7, 128.6, 128.5, 128.0, 126.7, 126.6, 45.2 (q, J = 27.4 Hz), 44.8 (q, J = 27.4 Hz), 21.3, 21.2, 20.9, 19.1, 18.5, 18.5. (mixture of two rotamers). ¹⁹F NMR (376.5 MHz, CDCl₃, CF₃CO₂H - ext. st.): δ (ppm) -69.2 (s, 2.2F - minor), -69.5 (s, 3F - major). HRMS (APPI⁺-Orbitrap) m/z : [M]⁺. Calcd for C₂₆H₂₅F₃ 394.1908; Found 394.1902 (-1.7 ppm).

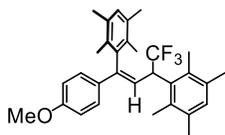


(*Z*)-6,6'-(4,4,4-Trifluoro-1-phenylbut-1-ene-1,3-diyl)bis(1,2,3,4,5-pentamethylbenzene) (**6h**) was prepared according to general procedure E from 1,1,1-trifluoro-4-phenylbut-3-yn-2-ol (50 μ L, 0.25 mmol) and pentamethylbenzene (111 mg, 0.75 mmol), with 2.2 μ L (0.025 mmol) of triflic acid, in 0.125 mL of HFIP (16 h, 50 °C). Purification by flash column chromatography over silica (petroleum ether) gave 114 mg (95% yield) of white solid. Mp: 183–185 °C. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.31–7.24 (m, 5H), 6.94 (d, J = 7.4 Hz, 1H), 4.53–4.43 (m, 1H), 2.41 (s, 3H), 2.27 (s, 3H), 2.25 (s, 3H), 2.21 (s, 3H), 2.20 (s, 3H), 2.16 (s, 3H), 2.02 (s, 3H), 1.82 (s, 3H), 1.29 (s, 3H), 0.84 (s, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ (ppm) 144.4, 140.0, 135.1, 134.8, 134.4, 134.0,

133.7, 133.4, 133.2, 132.9, 132.7, 132.4, 130.3, 129.7, 128.8, 127.8, 127.8 (q, $J = 280.5$ Hz), 126.2, 122.8, 46.2 (q, $J = 27.9$ Hz), 19.9, 19.8, 17.5, 17.4, 17.3, 17.1, 16.9, 16.8, 16.2, 15.9. ^{19}F NMR (376.5 MHz, CDCl_3 , $\text{CF}_3\text{CO}_2\text{H}$ - ext. st.): δ (ppm) -66.3 (s, 3F). HRMS (APPI⁺-Orbitrap) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{32}\text{H}_{38}\text{F}_3$ 479.2920; Found 479.2923 (0.6 ppm).



(*Z*)-6,6'-(4,4,4-Trifluoro-1-(*p*-tolyl)but-1-ene-1,3-diyl)bis(1,2,3,4,5-pentamethylbenzene) (**6i**) was prepared according to general procedure E from 1,1,1-trifluoro-4-(*p*-tolyl)but-3-yn-2-ol (53 mg, 0.25 mmol) and pentamethylbenzene (111 mg, 0.75 mmol), with 2.2 μL (0.025 mmol) of triflic acid, in 0.125 mL of HFIP (16 h, 50 $^\circ\text{C}$). Purification by flash column chromatography over silica (petroleum ether) gave 108 mg (88% yield) of white solid. Mp: 206–209 $^\circ\text{C}$. ^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.19 (d, $J = 8.2$ Hz, 2H), 7.09 (d, $J = 8.1$ Hz, 2H), 6.89 (d, $J = 7.4$ Hz, 1H), 4.52–4.41 (m, 1H), 2.39 (s, 3H), 2.33 (s, 3H), 2.27 (s, 3H), 2.21 (s, 3H), 2.19 (s, 3H), 2.15 (s, 3H), 2.02 (s, 3H), 1.82 (s, 3H), 1.29 (s, 3H), 0.84 (s, 3H), 0.09 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ (ppm) 144.2, 137.7, 137.2, 135.1, 134.9, 134.4, 133.9, 133.7, 133.4, 133.2, 132.8, 132.7, 132.0, 130.3, 129.8, 129.5, 127.8 (q, $J = 281.1$ Hz), 126.1, 121.8, 46.2 (q, $J = 27.8$ Hz), 21.4, 19.9, 19.8, 17.5, 17.4, 17.2, 17.0, 16.9, 16.8, 16.2, 15.9. ^{19}F NMR (376.5 MHz, CDCl_3 , $\text{CF}_3\text{CO}_2\text{H}$ - ext. st.): δ (ppm) -66.3 (s, 3F). HRMS (APPI⁺-Orbitrap) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{33}\text{H}_{39}\text{F}_3$ 492.2998; Found 492.3005 (1.2 ppm).



(*Z*)-3,3'-(4,4,4-Trifluoro-1-(4-methoxyphenyl)but-1-ene-1,3-diyl)bis(1,2,4,5-tetramethylbenzene) (**6j**) was prepared according to general procedure E from 1,1,1-trifluoro-4-(4-methoxyphenyl)but-3-yn-2-ol (58 mg, 0.25 mmol) and durene (102 mg, 0.75 mmol), with 2.2 μL (0.025 mmol) of triflic acid, in 0.125 mL of HFIP (16 h, 50 $^\circ\text{C}$). Purification by flash column chromatography over silica (petroleum ether/EtOAc 98:2) gave 65 mg (54% yield) of white solid. Mp: 144–146 $^\circ\text{C}$. ^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.19 (d, $J = 8.8$ Hz, 2H), 6.89 (s, 1H), 6.83 (d, $J = 7.9$ Hz, 2H), 6.81 (d, $J = 8.8$ Hz, 2H), 4.52–4.35 (m, 1H), 3.78 (s, 3H), 2.36 (s, 3H), 2.27 (s, 3H), 2.15 (s, 3H), 2.11 (s, 3H), 2.06 (s, 3H), 1.88 (s, 3H), 1.22 (s, 3H), 0.89 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ (ppm) 159.6, 143.4, 137.7, 135.7, 134.8, 134.4, 134.1, 133.9, 133.8, 133.4, 133.3, 131.9, 131.2, 130.6, 130.4, 127.5 (q, $J = 281.1$ Hz), 127.2, 119.9, 110.2, 55.4, 45.9 (q, $J = 27.8$ Hz), 21.4, 21.1, 20.5, 19.9, 19.7, 18.6, 16.1, 15.4, 14.9. ^{19}F NMR (376.5 MHz, CDCl_3 , $\text{CF}_3\text{CO}_2\text{H}$ - ext. st.): δ (ppm) -66.3 (s, 3F). HRMS (APPI⁺-Orbitrap) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{31}\text{H}_{35}\text{OF}_3$ 480.2635; Found 480.2636 (0.4 ppm).

ASSOCIATED CONTENT

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/xxxxxxxxx.

X-ray crystallography data of **1s** (CIF) and **6a** (CIF).

^1H and $^{13}\text{C}\{^1\text{H}\}$, and ^{19}F NMR spectra for the products (PDF).

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Notes

The authors declare no competing financial interest.

CCDC 1960543 and 1960571 contain the supplementary crystallographic data for this paper.

These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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