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Reaction of 1,2-Unsaturated Trifluoromethyl Ketones and Their Conversion to 1-(Trifluoromethyl)furan Derivatives

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A novel synthetic approach leading to 1-(trifluoromethyl)furan derivatives is reported. 4-Aryl-1,1,1-trifluorobut-3-en-2-one was iodinated and subsequently reduced to give the corresponding alcohol. The resultant iodo compound was then subjected to coupling with phenylacetylene to furnish an (*E*)-3-aryl-2-(2-phenylethynyl)-1-(trifluoromethyl)allyl alcohol, which could be cyclized by means of AgOTf to furnish a 2-(trifluoromethyl)furan in fair yield.

Introduction

As reported by Uneyama, *N*-substituted trifluoroacetimidoyl chloride is a trifluoromethyl building block for fluorinated nitrogen heterocycles.[1] We demonstrated that in addition to (trifluoromethyl)imidazole and -triazole derivatives,[2] this precursor was applied successfully for the asymmetric synthesis of trifluoromethylated 1- or 2-aminophosphonic acids by a 1,3-proton shift reaction, which represents a reducing agent free, biomimetic, reductive amination.[3] Moreover, a facile synthetic protocol for the formation of 1,2-unsaturated trifluoromethyl ketones was introduced by us.[4] This new and convenient one-pot procedure is based on the reaction of the anion derived from alkylphosphonates with *N*-phenyltrifluoroacetimidoyl chloride followed by a reaction with an aldehyde and acid hydrolysis. Since it is well documented that 1,2-unsaturated ketones are a class of reactive intermediates that give Michael addition and/or aldol condensation products through 1,4- or 1,2-addition, respectively, with various nucleophiles, the chemical behaviour of this trifluoromethylated 1,2-unsaturated ketone attracted our interest. As a result of this investigation, we have found a synthetic method leading to a 2-(trifluoromethyl)furan derivative with potential biological significance. The synthetic strategy used in this method is helpful for the preparation of biologically active small molecules and for their structural modifications as well.

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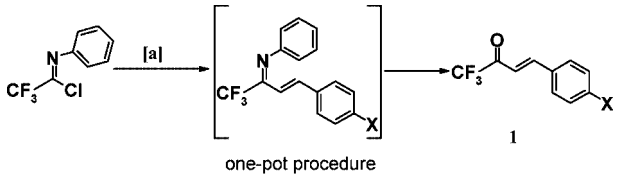
Results and Discussion

First of all, the preparation of 1,2-unsaturated trifluoromethyl ketones reported by us[4] was re-examined in order to optimize the reaction conditions and to investigate the scope of this procedure (Scheme 1).



X = H, CH_3, OCH_3, $N(CH_3)_2$, F, Cl, CN, *p*-NO_2, *m*-NO_2

Scheme 1. Reagents and reaction conditions: [a] LDA (2 equiv.), –70 °C; then $CH_3P(O)(OEt)_2$/ArCHO; then 2 N HCl, 4 h.

As shown in Table 1, substrates bearing either electron-withdrawing or electron-donating aryl substituents are accommodated well in this reaction, giving good to excellent yields. This method turns out to be practical and efficient for the preparation of various 1,2-unsaturated trifluoromethyl ketones. Compounds **1c** and **1f** were previously reported to be prepared by the reaction of 1,1,1-trifluoroacetaldehyde with *p*-substituted benzaldehydes.[5] Compound **1d** was prepared by the reaction of 1,2-unsaturated-3-methoxyethyl trifluoromethyl ketone with *N*,*N*-dimethylaniline in the presence of $ZnCl_2$ in CH_2Cl_2.[6] Compound **1g** was prepared in a similar manner.[7] Our method is much better than these since, in our case, the starting materials are easily available and the reaction conditions are milder, offering good yields. The spectroscopic data are reported in the electronic supporting information.

For the study of the chemical behaviour of **1**, our preliminary attention was paid to the reaction of **1** with various nucleophiles including nitroacetonitrile, ethoxyethene, 1-

Table 1. Preparation of 1,2-unsaturated trifluoromethyl ketones.

Entry	Compound	X	% Yield[a]
1	**1a**	H	85 (59)
2	**1b**	CH_3	80 (63)
3	**1c**	OCH_3	84
4	**1d**	$N(CH_3)_2$	72
5	**1e**	F	79 (72)
6	**1f**	Cl	79
7	**1g**	CN	67
8	**1h**	*p*-NO_2	81 (59)
9	**1i**	*m*-NO_2	94

[a] Yields of the products indicated in brackets were reported by us previously.[4] The reported yields were significantly increased by more carefully following the procedure.

(trimethylsiloxy)cyclohexene, 1-cyclohex-1-enyl piperidine, cyclohexanone, diethyl phosphite, trifluoroacetoacetate and trifluoro-2,4-dioxopentylphosphonate under Michael addition reaction conditions. Unfortunately, all of these trials failed as shown by the formation of inseparable mixtures instead of the desired 1,4-addition products. These results could be rationalized by the presence of the trifluoromethyl group in this conjugated 1,2-unsaturated ketone system. After we having finished this experimental work, a similar phenomenon was reported by Nenejdenko et al. who showed that trifluoromethyl enones gave 1,4-conjugated-addition products with ethyl nitroacetate only under special reaction conditions, that is in the presences of calcinated potassium fluoride as the base.[8] On the other hand, as found by us, compound **1** underwent smoothly an aldol condensation with acetone. This 1,2-addition was shown to be an enantioselective process, when L-proline was used as the catalyst. This result will be reported by us elsewhere in due course.[9]

Here we wish to describe a novel synthetic protocol for the preparation of 2-(trifluoromethyl)furans through the following sequences of the reactions, starting from 1,2-unsaturated trifluoromethyl ketones.

Compound **1** was transformed into the corresponding 1-iodinated intermediate **2** by I_2 in pyridine. Iodination proceeded smoothly at room temperature, and 48 h was usually required for the completion of the reaction. The yield of the iodination was quite satisfactory (Table 2).

Table 2. α-Iodination of 1,2-unsaturated trifluromethyl ketones.[a]

Entry	Compound	X	% Yield[b]
1	**2a**	H	72
2	**2b**	CH_3	83
3	**2c**	OCH_3	80
4	**2d**	$N(CH_3)_2$	–[c]
5	**2e**	F	92
6	**2f**	Cl	72
7	**2g**	CN	68
8	**2h**	*p*-NO_2	55
9	**2i**	*m*-NO_2	65

[a] Compounds **1** were stirred under a N_2 atmosphere in CCl_4/pyridine, treated with I_2/CCl_4/pyridine and stirred for 48 h at room temperature. [b] Isolated yields based on compound **1**. [c] Ref.[10], the product is unstable.

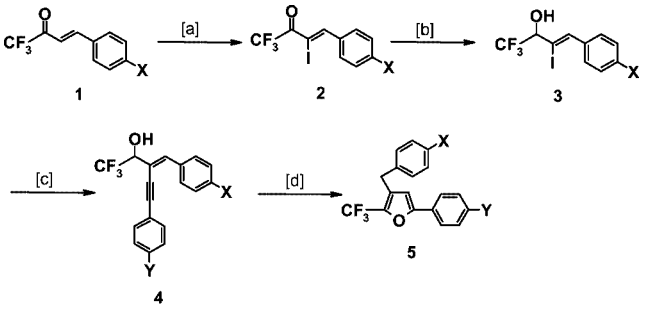
In order to eliminate the influence of the trifluoromethyl group through the conjugated system on the coupling reaction, **2** was reduced by the Luche method. It was quite successful, since all the sensitive groups in the substrates remained unchanged (Table 3).

Table 3. Reduction of compound **2**.[a]

Entry	Compound	X	% Yield[b]
1	**3a**	H	77
2	**3b**	CH_3	93
3	**3c**	OCH_3	85
4	**3d+3d′**	$N(CH_3)_2$	48.5 and 22.1[c]
5	**3e**	F	92
6	**3f**	Cl	90
7	**3g**	CN	85
8	**3h**	*p*-NO_2	>99
9	**3i**	*m*-NO_2	62

[a] Reduction occurred smoothly with $NaBH_4$. [b] Isolated yields based on compounds **2**. [c] Ref.[10].

Compounds **3** are useful synthetic precursors in which the strong electronic influence of the trifluoromethyl carbonyl group on the double bond is eliminated. Coupling of **3** with phenylacetylene catalyzed by transition metals turned out to be successful (Scheme 2), providing good to excellent yields (Table 4). During the period of the study on this reaction, we also found that $Pd(PPh_3)_4$ and CuI together with triethylamine were more effective than $[PdCl_2(PPh_3)_2]$, the classical catalyst in Sonogashira coupling reactions.[11]



X = H, CH_3, OCH_3, $N(CH_3)_2$, F, Cl, CN, *p*-NO_2, *m*-NO_2; Y = H, Cl

Scheme 2. Reagents and reaction conditions: [a] I_2, pyridine, CCl_4; [b] $NaBH_4$, $CeCl_3{\cdot}7H_2O$, CH_3OH; [c] $YC_6H_4C{\equiv}CH$, $Pd(PPh_3)_4$, CuI and NEt_3, 50 °C under Ar; [d] 5 mol-% AgOTf, CH_2ClCH_2Cl, 80 °C.

The unique structure of **4** makes it a very promising building block for the synthesis of polysubstituted furans. Previously, a variety of synthetic methods leading to polysubstituted furans was reported including the cyclization of 3-alkynyl allylic alcohols under basic conditions[12] or catalyzed by Ru[13] or Pd.[14] Recently, Qing's group reported the synthesis of trifluoroethylfurans by a Pd-catalyzed cyclization.[11] However, they failed to obtain trifluoromethyl-substituted furan derivatives by this strategy.[15] Since polysubstituted furans have potential biological activities and could be used as building blocks in natural-product synthesis, our attention was paid to realizing the formation of them starting from **4**.

Table 4. Pd-catalyzed reaction of **3** with terminal alkynes.[a]

Entry	Compound	X	Y	% Yield[b]
1	**4a**	H	H	82
2	**4b**	CH_3	H	84
3	**4c**	OCH_3	H	>99
4	**4d**	F	H	97
5	**4e**	Cl	H	88
6	**4f**	CN	H	88
7	**4g**	*p*-NO_2	H	94
8	**4h**	*m*-NO_2	H	89
9	**4i**	H	Cl	88
10	**4j**	CH_3	Cl	87
11	**4k**	$N(CH_3)_3$	Cl	80
12	**4l**	F	Cl	83
13	**4m**	Cl	Cl	82
14	**4n**	CN	Cl	84
15	**4o**	*p*-NO_2	Cl	85
16	**4p**	*m*-NO_2	Cl	83

[a] The Sonogashira coupling process was modified: under Ar, a mixture of **3**, $Pd(PPh_3)_4$ and CuI was stirred and then followed by the addition of Et_3N and phenylacetylene. [b] Isolated yields based on compounds **3**.

Our initial attempts at the conversion of **4** to **5** were focused on catalytic cyclization. It was not easy to select an effective catalyst system. As found by us, even when $[PdCl_2(PPh_3)_2]$ was used, only a 25% yield was obtained in a low-polarity solvent such as cyclohexane. We assumed that the low reaction yield may be associated with the reduction of Pd as shown by the formation Pd^0 as black precipitates during the reaction. The reductive process could not be reversed simply by the addition of an equiv. of an oxidant such as $Cu(OAc)_2$. It is interesting to note that when the aprotic solvent THF or diisopropyl ether was applied as solvent, a small amount of dihydrofuran could be obtained. However, in most cases, furans were obtained as the main products. When other metal salts, such as $NaAuCl_4{\cdot}4H_2O$ and $Cu(OAc)_2$, were used, only an inseparable mixture was obtained. We also examined the reactivity of $AgNO_3$ loaded on silica gel, but the result was also not encouraging.

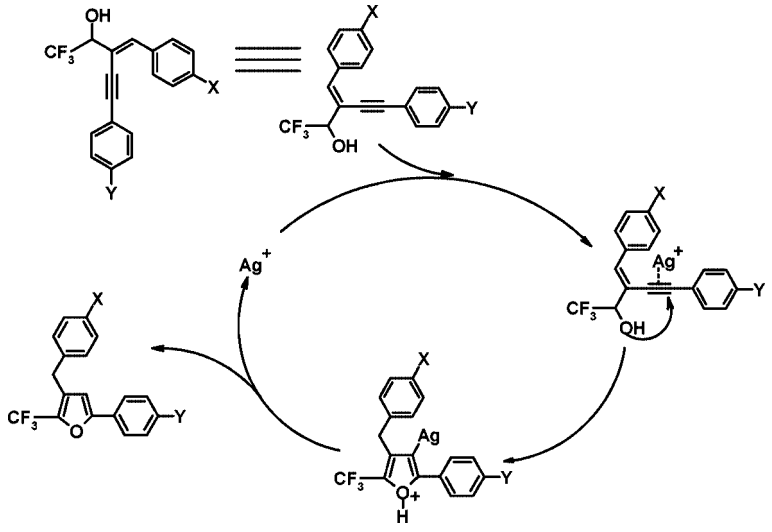
After a series of efforts, we found that a AgOTf-catalyzed intramolecular reaction[16] was fully satisfactory for our purpose. It is well known that Ag^I-catalyzed cyclization reactions have been widely applied for a number of years.[17] However, we found that the commonly used $AgNO_3$ on silica gel had no effect on this reaction, as mentioned above. At room temperature, AgOTf did not catalyze the reaction either. However, when we tried the conditions given in the literature, to our delight, this catalytic system showed high activity under conditions. Most substrates were converted smoothly to the expected 1-trifluoromethylfurans in good to excellent yields (Table 5). We ascribed this mainly to the use of $ClCH_2CH_2Cl$ as solvent, which has a relatively high boiling point.

Table 5. Cyclization of **4** to α-(trifluoromethyl)furans catalyzed by AgOTf.[a]

Entry	Compound	X	Y	% Yield[b]
1	**5a**	H	H	68
2	**5b**	CH_3	H	71
3	**5c**	OCH_3	H	[c]
4	**5d**	F	H	81
5	**5e**	Cl	H	49
6	**5f**	CN	H	84
7	**5g**	*p*-NO_2	H	91
8	**5h**	*m*-NO_2	H	79[a]
9	**5i**	H	Cl	65
10	**5j**	CH_3	Cl	66
11	**5k**	$N(CH_3)_2$	Cl	[c]
12	**5l**	F	Cl	71
13	**5m**	Cl	Cl	78
14	**5n**	CN	Cl	89[a]
15	**5o**	*p*-NO_2	Cl	76[a]
16	**5p**	*m*-NO_2	Cl	>99[a]

[a] The reaction took 48 h and 10 mol-% AgOTf was used, while in other reaction system 5 mol-% AgOTf was used, and 24 h were required for the reaction. [b] Isolated yield based on compound **4**. [c] As indicated by TLC, the reaction products are very complicated; this is rationalized in the text.

The data in Table 5 demonstrate that substrates bearing an electron-donating group (**5c** and **5k**) were inactive in this



Scheme 3. A tentatively proposed catalytic cycle for the formation of **5**.

reaction system. We supposed that the high electron density of the substrates deactivated the catalytic capacity of AgOTf by decomposition. Actually we indeed found some black residue of silver in the reaction flask. It should also be noted that substrates with electron-withdrawing groups reacted more slowly than those bearing electron-donating groups, though they provided pretty high yields. To clarify this dilemma, we should first have a look at the plausible mechanism of this cyclization (Scheme 3). In this mechanism, AgOTf, acting as a Lewis acid, coordinates to the triple bond, which greatly enhances the electrophilicity of the latter moiety. However, the process is relatively difficult for substrates bearing electron-withdrawing groups because of their electron-deficiency. As a result, these substrates usually react more slowly compared to others. But once this process is complete, the more electron-deficient property would make the hydroxyl group attack on the triple bond easier, leading to the irreversibility of this reaction. Therefore, it could be observed that yields are still high, although the reaction rate seems slow.

To further confirm the configuration of the resulting α-(trifluoromethyl)furans, compound **5h** was examined by a single-crystal X-ray analysis (see Figure 1).

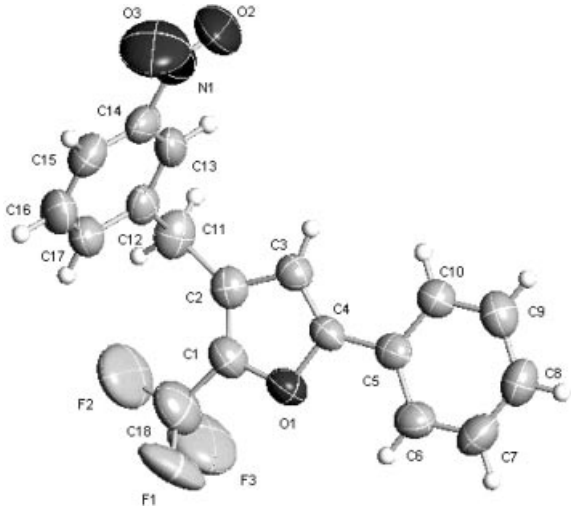


Figure 1. Crystal structure of compound **5h**.

Conclusions

An efficient synthesis leading to α-(trifluoromethyl)furans has been developed starting from the readily available 1,2-unsaturated trifluoromethyl ketones. Additionally, several reactive intermediates with potential applications in organic synthesis, such as 1-iodinated 1,2-unsaturated trifluoroalkyl ketones and halogenated allylic alcohols, are described.

Experimental Section

General Remarks: All reactions were performed under a N_2 or Ar atmosphere. Dichloromethane, *i*Pr_2NH, and Et_3N were distilled from CaH_2 under N_2. THF was freshly distilled from sodium under N_2 prior to use. Other reagents were purified by standard methods.[18] Column chromatography was performed with silica gel (300–400 mesh). ^1H NMR (300 MHz) and ^{19}F NMR (282 MHz) were recorded on a 300-MHz spectrometer with $CDCl_3$ as the solvent and tetramethylsilane (TMS) as the internal standard. Chemical shifts (δ) are reported in ppm relative to TMS. ^{19}F NMR was performed with CF_3COOH as the external standard, downfield shifts being designated as negative. IR spectra were obtained with a Shimadzu IR-440 spectrometer. Mass spectra were obtained using EI ionization at 70 eV. All reactions were routinely monitored by TLC.

General Procedure for Preparation of α,β-Unsaturated Trifluoromethyl Ketones 1: To a stirred solution of *i*Pr_2NH (20 mmol, 3.2 mL) in dry THF (40 mL) was added dropwise *n*BuLi (1.6 M in hexane; 20 mmol, 12.5 mL) at –78 °C. After 20 min, $CH_3P(O)(OEt)_2$ (10 mmol, 1.5 mL) was added. After the mixture was stirred for 30 min at the same temperature, *N*-phenyltrifluoroacetimidyl chloride (10 mmol, 1.60 mL) was gradually added with stirring, and then the reaction mixture was kept at –70 °C for 1 h. A solution of substituted benzaldehyde (10 mmol, 1.51 g) in dry THF (10 mL) was then added dropwise, and the temperature was maintained below –60 °C. The resulting mixture was then warmed to room temperature over 2 h and stirred overnight. After the addition of 2 N HCl (20 mL) to the mixture, it was stirred at room temperature for another 4 h and then extracted with diethyl ether (3 × 20 mL). The combined extracts were washed successively with 5% aq $NaHCO_3$ and brine until pH 6 was reached, and the organic solution obtained was dried with anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was subjected to flash chromatography on silica gel (hexane/EtOAc = 5:1 to 20:1) to afford pure **1**.

1,1,1-Trifluoro-4-phenylbut-3-en-2-one (1a): Yellow oil, 1.71 g, 85% yield. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.97 (d, $^3J_{H,H}$ = 16.2 Hz, 1 H, CH=CH), 7.66–7.42 (m, 5 H, Ar-H), 7.02 (d, $^3J_{H,H}$ = 16.2 Hz, 1 H, CH=CH) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –77.6 (s, 3 F, CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 1721, 1612, 1600, 1578, 1452, 1266, 1147, 1059 cm^{-1}. EI-MS: *m*/*z* (%) = 200 (6) $[M]^+$, 57 (100).

1,1,1-Trifluoro-4-(4-methylphenyl)but-3-en-2-one (1b): Light yellow oil, 1.72 g, 80.2% yield. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.88 (d, $^3J_{H,H}$ = 15.9 Hz, 1 H, CH=CH), 7.47 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H, Ar-H), 7.18 (d, ^3J = 8.4 Hz, 2 H, Ar-H), 6.90 (d, $^3J_{H,H}$ = 15.9 Hz, 1 H, CH=CH), 2.34 (s, 3 H, CH_3) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –77.5 (s, 3 F, CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 1712, 1688, 1602, 1599, 1515, 1268, 1199, 1146, 1059 cm^{-1}. EI-MS: *m*/*z* (%) = 214 (31) $[M]^+$, 145 (100).

1,1,1-Trifluoro-4-(4-fluorophenyl)but-3-en-2-one (1e): Light yellow solid, 1.72 g, 79% yield. M.p. 48–50 °C. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.93 (d, $^3J_{H,H}$ = 15.9 Hz, 1 H, CH=CH), 7.68–7.63 (m, 2 H, Ar-H), 7.15 (t, $^3J_{H,H}$ = 8.1 Hz, 2 H, Ar-H), 6.94 (d, $^3J_{H,H}$ = 15.9 Hz, 1 H, CH=CH) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –77.6 (s, 3 F, CF_3), –105.6 (m, 1 F) ppm. IR (KBr): $\tilde{\nu}$ = 1712, 1612, 1590, 1510, 1420, 1323, 1266, 1160, 1141, 1056 cm^{-1}. EI-MS: *m*/*z* (%) = 218 (36) $[M]^+$, 149 (100).

1,1,1-Trifluoro-4-(4-nitrophenyl)-but-3-en-2-one (1h): Yellow solid, 2.00 g, 81% yield. M.p. 98–99 °C. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.32 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H, Ar-H), 7.99 (d, $^3J_{H,H}$ = 15.9 Hz, 1 H, CH=CH), 7.83 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H, Ar-H), 7.14 (d, $^3J_{H,H}$ = 15.9 Hz, 1 H, CH=CH) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –77.7 (s, 3 F, CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 3082,

1722, 1616, 1593, 1346, 1266, 1056 cm^{-1}. EI-MS: *m*/*z* (%) = 245 (6) [M]$^+$, 102 (100).

General Procedure for Preparation of α-Iodo α,β-Unsaturated Trifluoromethyl Ketones 2: To a stirred solution of **1** (10 mmol) in CCl_4/pyridine (1:1, 40 mL) was added dropwise a solution of I_2 (7.62 g, 30 mmol) in CCl_4/pyridine (1:1, 40 mL) under an atmosphere of N_2 at 0 °C. The resulting mixture was then warmed to room temperature and stirred for 48 h. Then 1 N HCl (100 mL) was added, and the mixture was extracted with diethyl ether (3 × 50 mL). The combined organic layers were washed with 1 N HCl until the pH turned acidic (approximately 4), and the layers were treated with saturated aq $NaHCO_3$ until neutral (this was especially essential since it facilitated layer separation). The organic layers were again washed successively with saturated aqueous $Na_2S_2O_3$ and H_2O, after which they were dried with anhydrous Na_2SO_4 overnight and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel (hexane/EtOAc = 5:1 to 20:1) to afford pure **2**.

1,1,1-Trifluoro-3-iodo-4-phenylbut-3-en-2-one (2a): Dark red oil 2.35 g, 72% yield. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.23 (s, 1 H, =CH), 7.91–7.47 (m, 5 H, Ar-H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –67.9 (s, 3 F, CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 1711, 1588, 1570, 1448, 1305, 1204, 1149, 1112 cm^{-1}. EI-MS: *m*/*z* (%) = 326 (8) [M]$^+$, 102 (100). HRMS: calcd. for $C_{10}H_6F_3IO$ 325.9416; found 325.9424.

1,1,1-Trifluoro-3-iodo-4-(4-methylphenyl)but-3-en-2-one (2b): Dark red oil, 2.82 g, 83% yield. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.22 (s, 1 H, =CH), 7.87 (d, J = 8.4 Hz, 2 H, Ar-H), 7.31 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H, Ar-H), 2.43 (s, 3 H, CH_3) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –67.7 (s, 3 F, CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 3030, 1706, 1608, 1583, 1562, 1303, 1203, 1149, 1105 cm^{-1}. EI-MS: *m*/*z* (%) = 340 (45) [M]$^+$, 116 (100). HRMS: calcd. for $C_{11}H_8F_3IO$ 339.9572; found 339.9572.

1,1,1-Trifluoro-3-iodo-4-(4-methoxyphenyl)but-3-en-2-one (2c): Dark red oil, 2.85 g, 80% yield. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.21 (s, 1 H, =CH), 8.05 (d, $^3J_{H,H}$ = 8.7 Hz, 2 H, Ar-H), 7.02 (d, $^3J_{H,H}$ = 8.7 Hz, 2 H, Ar-H), 3.90 (s, 3 H, OCH_3) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –67.5 (s, 3 F, CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 3075, 2904, 2844, 1700, 1605, 1581, 1560, 1427, 1373, 1263, 1179, 1029 cm^{-1}. EI-MS: *m*/*z* (%) = 356 (8) [M]$^+$, 132 (100). HRMS: calcd. for $C_{11}H_8F_3IO_2$ 355.9521; found 325.9525.

1,1,1-Trifluoro-3-iodo-4-(4-fluorophenyl)but-3-en-2-one (2e): Dark red oil, 3.16 g, 92% yield. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.20 (s, 1 H, =CH), 7.96 (d, $^3J_{H,H}$ = 5.4 Hz, 1 H, Ar-H), 7.48 (d, $^3J_{H,H}$ = 5.4 Hz, 1 H, Ar-H), 7.21 (t, $^3J_{H,H}$ = 13 Hz, 2 H, Ar-H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –67.9 (s, 3 F, CF_3), –105.6 (m, 1 F) ppm. IR (KBr): $\tilde{\nu}$ = 3079, 2928, 1711, 1597, 1509, 1303, 1242, 1162, 1097 cm^{-1}. EI-MS: *m*/*z* (%) = 344 (29) [M]$^+$, 40 (100). HRMS: calcd. for $C_{10}H_5F_4IO$ 343.9321; found 343.9319.

4-(4-Chlorophenyl)-1,1,1-trifluoro-3-iodobut-3-en-2-one (2f): Yellow solid, 2.60 g, 72% yield. M.p. 73–75 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.18 (s, 1 H, =CH), 7.85 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H, Ar-H), 7.48 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H, Ar-H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –67.9 (s, 3 F, CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 3095, 1698, 1582, 1491, 1411, 1201, 1155, 1091, 1010 cm^{-1}. EI-MS: *m*/*z* (%) = 360 (3.9) [M]$^+$ 136 (100). $C_{10}H_5ClF_3IO$ (360.50): calcd. C 33.32, H 1.40; found C 33.47, H 1.36.

4-(4-Cyanophenyl)-1,1,1-trifluoro-3-iodobut-3-en-2-one (2g): Yellow solid, 2.39 g, 68% yield. M.p. 80–81 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.20 (s, 1 H, =CH), 7.89 (d, $^3J_{H,H}$ = 8.7 Hz, 2 H, Ar-H), 7.78 (d, $^3J_{H,H}$ = 8.7 Hz, 2 H, Ar-H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –68.2 (s, 3 F, CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 2227, 1707, 1581, 1415, 1300, 1199, 1158, 1094 cm^{-1}. EI-MS: *m*/*z* (%) = 351 (24) [M]$^+$, 127 (100). $C_{11}H_5F_3INO$ (351.07): calcd. C 37.63, H 1.44, N 3.99; found C 37.79, H 1.54, N 4.00.

1,1,1-Trifluoro-3-iodo-4-(4-nitrophenyl)but-3-en-2-one (2h): Yellow solid, 2.04 g, 55% yield. M.p. 73–74 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.35 (d, $^3J_{H,H}$ = 9.0 Hz, 2 H, Ar-H), 8.24 (s, 1 H, =CH) 7.93 (d, $^3J_{H,H}$ = 9.0 Hz, 2 H, Ar-H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –68.3 (s, 3 F, CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 3108, 1709, 1603, 1573, 1523, 1414, 1342, 1202, 1158, 1093 cm^{-1}. EI-MS: *m*/*z* (%) = 371 (3) [M]$^+$, 57 (100). $C_{10}H_5ClF_3IO$ (371.06): calcd. C 32.37, H 1.36, N 3.77; found C 32.58, H 1.39, N 3.87.

1,1,1-Trifluoro-3-iodo-4-(3-nitrophenyl)but-3-en-2-one (2i): Yellow solid, 2.41 g, 65% yield. M.p. 70–71 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.73 (s, 1 H, Ar-H), 8.37 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H, Ar-H), 8.24 (s, 1 H, =CH), 8.11 (d, $^3J_{H,H}$ = 7.8 Hz, 1 H, Ar-H), 7.71 (t, $^3J_{H,H}$ = 7.5 Hz, 1 H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –68.1 (s, 3 F, CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 1702, 1589, 1532, 1444, 1352, 1277, 1164, 1101 cm^{-1}. EI-MS: *m*/*z* (%) = 371 (32) [M]$^+$, 302 (100). $C_{10}H_5F_3INO_3$ (371.06): calcd. C 32.37, H 1.36, N 3.77; found C 32.45, H 1.46, N 3.78.

General Procedure for Preparation of Halogenated Allylic Alcohols 3: To a solution of **2** (1 mmol) in CH_3OH (7.5 mL) was added $CeCl_3 \cdot 7H_2O$ (0.39 g, 1.05 mmol), and the solution was stirred for 10 min. $NaBH_4$ (38 mg, 1 mmol) was then added. After the gas release was over, the solution was stirred for another 30 min. Saturated aqueous NH_4Cl was added, and the solvent was removed under reduced pressure, after which H_2O was again added, and the mixture was extracted with diethyl ether (3 × 10 mL). The combined organic layers were washed with brine and dried with anhydrous Na_2SO_4 overnight. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography on silica gel (chloroform/hexane = 5:1 to 15:1) to afford pure **3**.

(Z)-1,1,1-Trifluoro-3-iodo-4-phenylbut-3-en-2-ol (3a): White solid 253 mg, 77% yield. M.p. 52–53 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.56–7.38 (m, 5 H, Ar-H), 7.35 (s, 1 H, =CH), 4.50 (m, 1 H, *CH*OH), 2.79 (d, $^3J_{H,H}$ = 8.4 Hz, 1 H, OH) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –75.9 (d, $^3J_{H,F}$ = 6.8 Hz, 3 F, CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 3323, 3026, 2725, 1624, 1496, 1446, 1254, 1174, 1079 cm^{-1}. EI-MS: *m*/*z* (%) = 328 (8) [M]$^+$, 132 (100). $C_{10}H_8F_3IO$ (328.07): calcd. C 36.61, H 2.46; found C 36.74, H 2.50.

(Z)-1,1,1-Trifluoro-3-iodo-4-(4-methylphenyl)but-3-en-2-ol (3b): White solid, 318 mg, yield: 93%. M.p.: 30–31 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.46 (d, $^3J_{H,H}$ = 7.8 Hz, 2 H, Ar-H), 7.29 (s, 1 H, =CH), 7.20 (d, $^3J_{H,H}$ = 7.8 Hz, 2 H, Ar-H), 4.46 (m, 1 H, *CH*OH), 2.84 (d, $^3J_{H,H}$ = 8.6 Hz, 1 H, OH), 2.36 (s, 3 H, CH_3) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –75.8 (d, $^3J_{H,F}$ = 6.5 Hz, 3 F, CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 3425, 3027, 2924, 1611, 1512, 1448, 1268, 1176, 1113, 1044 cm^{-1}. EI-MS: *m*/*z* (%) = 342 (11) [M]$^+$, 341 (100). $C_{11}H_{10}F_3IO$ (342.10): calcd. C 38.62, H 2.95; found C 38.80, H 3.01.

(Z)-1,1,1-Trifluoro-3-iodo-4-(4-methoxyphenyl)but-3-en-2-ol (3c): Orange oil, 304 mg, 85% yield. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.57 (d, $^3J_{H,H}$ = 12.0 Hz, 2 H, Ar-H), 7.27 (s, 1 H, =CH), 6.93 (d, $^3J_{H,H}$ = 12.0 Hz, 2 H, Ar-H), 4.46 (m, 1 H, *CH*OH), 3.84 (s, 3 H, OCH_3), 2.82 (s, 1 H, OH) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –75.9 (d, $^3J_{H,F}$ = 6.2 Hz, 3 F, CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 3441, 3007, 2912, 2841, 1607, 1511, 1464, 1255, 1179, 1031 cm^{-1}. EI-MS: *m*/*z* (%) = 358 (14) [M]$^+$, 357 (100). $C_{11}H_{10}F_3IO_2$ (358.10): calcd. C 36.90, H 2.81; found C 37.01, H 2.99.

(Z)-4-[4-(Dimethylamino)phenyl]-1,1,1-trifluoro-3-iodobut-3-en-2-ol (3d): Dark red solid, 180 mg, 48.5% yield. M.p. 53–56 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.53 (d, $^3J_{H,H}$ = 9.0 Hz, 2 H, Ar-H), 7.11 (s, 1 H, =CH), 6.62 (d, $^3J_{H,H}$ = 9.0 Hz, 2 H, Ar-H), 4.33 (m, 1 H, *CH*OH), 2.91 [s, 6 H, $N(CH_3)_2$], 2.82 (d, $^3J_{H,H}$ = 4.2 Hz, 1 H, OH) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –75.8 (d, $^3J_{H,F}$ = 5.6 Hz, 3 F, CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 3376, 2443, 1705, 1609, 1523, 1366, 1271, 1169, 1128, 1062 cm^{-1}. ESI-MS: *m*/*z* = 371.9 $[M + H]^+$, 390.0 $[M + CH_3OH + H]^+$. HRMS: calcd. for $C_{12}H_{13}F_3INO$ 370.9994; found 371.0003.

(Z)-1,1,1-Trifluoro-3-iodo-4-[4-(methylamino)phenyl]but-3-en-2-ol (3d′): Brown oil, 82 mg, 22.1% yield. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.56 (d, $^3J_{H,H}$ = 8.7 Hz, 2 H, Ar-H), 7.18 (s, 1 H, =CH), 6.60 (d, $^3J_{H,H}$ = 8.7 Hz, 2 H), 4.41 (q, $^3J_{H,H}$ = 6 Hz, 1 H, *CH*OH), 2.92 (s, 3 H, NH*CH*$_3$), 3.29 (br., 2 H, O*H*, N*H*CH_3) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –75.8 (d, $^3J_{H,F}$ = 5.6 Hz, 3 F, CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 3396, 1705, 1614, 1523, 1274, 1171, 1129 cm^{-1}. ESI-MS: *m*/*z* = 357.9 $[M + H]^+$, 404 $[M + CH_3OH + H]^+$.

(Z)-1,1,1-Trifluoro-4-(4-fluorophenyl)-3-iodobut-3-en-2-ol (3e): Light yellow oil, 318 mg, 92% yield. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.46 (dd, J_1 = 5.7 Hz, $^3J_{H,H}$ = 8.4 Hz, 2 H, Ar-H), 7.23 (s, 1 H, =CH), 7.02 (m, 2 H, Ar-H), 4.42 (m, 1 H, *CH*OH), 2.84 (s, 1 H, OH) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –75.8 (d, $^3J_{H,F}$ = 5.9 Hz, 3 F, CF_3), –111.3 (m, 1 F) ppm. IR (KBr): $\tilde{\nu}$ = 3440, 2923, 1897, 1624, 1603, 1509, 1413, 1268, 1180, 1098 cm^{-1}. EI-MS: *m*/*z* (%) = 346 (12) $[M]^+$, 345 (100). $C_{10}H_7F_4IO$ (346.06): calcd. C 34.71, H 2.04; found C 34.63, H 2.01.

(Z)-4-(4-Chlorophenyl)-1,1,1-trifluoro-3-iodobut-3-en-2-ol (3f): White solid, 326 mg, 90% yield. M.p. 92–95 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.48 (d, $^3J_{H,H}$ = 8.6 Hz, 2 H, Ar-H), 7.20 (d, $^3J_{H,H}$ = 8.6 Hz, 2 H, Ar-H), 7.30 (s, 1 H, =CH), 4.51 (m, 1 H, *CH*OH), 2.89 (d, *J* = 7.5 Hz, 1 H, OH) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –75.8 (d, $^3J_{H,F}$ = 6.5 Hz, 3 F, CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 3434, 2927, 1905, 1625, 1593, 1490, 1403, 1267, 1175, 1092 cm^{-1}. EI-MS: *m*/*z* (%) = 364 (2) $[M + 2]^+$, 363 (18), 262 (6) $[M]^+$, 261 (53), 294 (16), 292 (55), 174 (10), 131 (100), 101 (41), 75 (43), 69 (28), 63 (18), 51 (42), 41 (2). $C_{10}H_7ClF_3IO$ (362.52): calcd. C 33.13, H 1.95; found C 33.45, H 1.92.

(Z)-4-(4-Cyanophenyl)-1,1,1-trifluoro-3-iodobut-3-en-2-ol (3g): Yellow solid, 300 mg, 85% yield. M.p. 118–119 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.70 (d, $^3J_{H,H}$ = 8.1 Hz, 2 H, Ar-H), 7.62 (d, $^3J_{H,H}$ = 8.1 Hz, 2 H, Ar-H), 7.40 (s, 1 H, =CH), 4.59 (m, 1 H, *CH*OH), 2.98 (d, $^3J_{H,H}$ = 7.5 Hz, 1 H, OH) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –75.8 (d, $^3J_{H,F}$ = 6.2 Hz, 3 F, CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 3414, 2920, 2233, 1926, 1605, 1503, 1411, 1348, 1267, 1175, 1132, 1019 cm^{-1}. EI-MS: *m*/*z* (%) = 353 (77) $[M]^+$, 284 (100). $C_{11}H_7F_3INO$ (353.08): calcd. C 37.42, H 2.00, N 3.97; found C 36.99, H 2.21, N 3.79.

(Z)-1,1,1-Trifluoro-3-iodo-4-(4-nitrophenyl)but-3-en-2-ol (3h): Brown oil, 373 mg, >99% yield. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.27 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H, Ar-H), 7.68 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H, Ar-H), 7.45 (s, 1 H, =CH), 4.61 (m, 1 H, *CH*OH), 2.92 (d, $^3J_{H,H}$ = 6.6 Hz, 1 H, OH) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –75.8 (d, $^3J_{H,F}$ = 6.2 Hz, 3 F, CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 3464, 2983, 2854, 1596, 1519, 1347, 1267, 1177, 1130, 1014 cm^{-1}. EI-MS: *m*/*z* (%) = 373 (14) $[M]^+$, 131 (100). HRMS: calcd. for $C_{10}H_7F_3INO_3$ 372.9423; found 372.9424.

(Z)-1,1,1-Trifluoro-3-iodo-4-(3-nitrophenyl)but-3-en-2-ol (3i): Brown oil, 231 mg, 62% yield. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.42 (s, 1 H, Ar-H), 8.24 (d, $^3J_{H,H}$ = 8.4 Hz, 1 H, Ar-H), 7.84 (d, $^3J_{H,H}$ = 7.5 Hz, 1 H, Ar-H), 7.60 (t, $^3J_{H,H}$ = 7.8 Hz, 1 H, Ar-H), 7.43 (s, 1 H, =CH), 4.62 (m, 1 H, *CH*OH), 3.00 (d, *J* = 7.5 Hz, 1 H, OH) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –75.8 (d, $^3J_{H,F}$ = 6.5 Hz, 3 F, CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 3469, 3088, 2926, 1616, 1529, 1354, 1267, 1177, 1130 cm^{-1}. EI-MS: *m*/*z* (%) = 373 (49) $[M]^+$, 102 (100). $C_{10}H_7F_3INO_3$ (373.07): calcd. C 32.20, H 1.89, N 3.75; found C 32.28, H 2.09, N 3.70.

General Procedure for Preparation of Allylic Alcohols 4: To a 25-mL flask purged with Ar was added **3** (1 mmol), $Pd(PPh_3)_4$ (57.5 mg, 0.05 mmol, 5 mol-%) and CuI (19.1 mg, 0.1 mmol, 10 mol-%). Distilled Et_3N (6 mL) was then added dropwise to the solution. After stirring for 30 min, phenylacetylene (0.17 mL, 153 mg, 1.5 mmol) was added slowly into the mixture. The reaction system was then warmed to 40–50 °C and kept at that temperature for 12 h. The mixture was filtered, and the filtrate was extracted with diethyl ether (3 × 10 mL) and dried with anhydrous Na_2SO_4 overnight. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography on silica gel (chloroform/hexane = 5:1 to 15:1) to afford pure **4**.

(*E*)-1,1,1-Trifluoro-4-phenyl-3-(2-phenylethynyl)but-3-en-2-ol (4a): White solid, 248 mg, 82% yield. M.p. 77–78 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.93 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H, Ar-H), 7.53–7.34 (m, 8 H, Ar-H), 6.96 (s, 1 H, =CH), 4.64 (m, 1 H, CF_3CH), 2.84 (d, $^3J_{H,H}$ = 9.0 Hz, 1 H, OH) ppm. ^{19}F NMR: δ = –77.5 (d, $^3J_{H,F}$ = 6.6 Hz, 3 F, CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 3479, 3088, 3067, 2195, 1607, 1491, 1251, 1190, 1116, 1074 cm^{-1}. EI-MS: *m*/*z* (%) = 302 (4) $[M]^+$, 105 (100). $C_{18}H_{13}F_3O$ (302.30): calcd. C 71.52, H 4.33; found C 71.28, H 4.41.

(*E*)-1,1,1-Trifluoro-4-(4-methylphenyl)-3-(2-phenylethynyl)but-3-en-2-ol (4b): Light yellow oil, 265 mg, 84% yield. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.74 (d, $^3J_{H,H}$ = 7.8 Hz, 2 H, Ar-H), 7.43–7.27 (m, 5 H, Ar-H), 7.13 (d, $^3J_{H,H}$ = 7.8 Hz, 2 H, Ar-H), 6.62 (s, 1 H, =CH), 4.53 (q, $^3J_{H,H}$ = 5.1 Hz, 1 H, CF_3CH), 2.83 (br., 1 H, OH), 2.29 (s, 3 H, CH_3) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –77.5 (d, $^3J_{H,F}$ = 5.1 Hz, 3 F, CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 3451, 3032, 2925, 2199, 1608, 1512, 1491, 1443, 1270, 1171, 1069 cm^{-1}. EI-MS: *m*/*z* (%) = 316 (26) $[M]^+$, 204 (26), 105 (100), 91 (16), 77 (19), 63 (9), 51 (18). $C_{19}H_{15}F_3O$ (316.33): calcd. C 72.14, H 4.78; found C 72.56, H 4.98.

(*E*)-1,1,1-Trifluoro-4-(4-methoxyphenyl)-3-(2-phenylethynyl)but-3-en-2-ol (4c): Yellow solid, 332 mg, >99% yield. M.p. 80–83 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.91 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H, Ar-H), 7.54–7.34 (m, 5 H, Ar-H), 6.93 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H, Ar-H), 6.86 (s, 1 H, =CH), 4.60 (m, 1 H, CF_3CH), 3.85 (s, 3 H, OCH_3), 2.83 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H, OH) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –77.6 (d, $^3J_{H,F}$ = 7.2 Hz, 3 F, CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 3449, 3082, 2841, 2198, 1604, 1512, 1491, 1443, 1259, 1178, 1070 cm^{-1}. EI-MS: *m*/*z* (%) = 332 (18) $[M]^+$, 105 (100). $C_{19}H_{15}F_3O_2$ (332.33): calcd. C 68.67, H 4.55; found C 68.44, H 4.32.

(*E*)-1,1,1-Trifluoro-4-(4-fluorophenyl)-3-(2-phenylethynyl)but-3-en-2-ol (4d): White solid, 310 mg, 97% yield. M.p. 79–80 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.93 (t, $^3J_{H,H}$ = 7.5 Hz, 2 H, Ar-H), 7.52–7.38 (m, 5 H, Ar-H), 7.10 (t, $^3J_{H,H}$ = 8.7 Hz, 2 H, Ar-H), 6.93 (s, 1 H, =CH), 4.64 (m, 1 H, CF_3CH), 2.83 (d, $^3J_{H,H}$ = 8.4 Hz, 1 H, OH) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –77.5 (d, $^3J_{H,F}$ = 6.3 Hz, 3 F, CF_3), –110.3 (m, 1 F) ppm. IR (KBr): $\tilde{\nu}$ = 3474, 3039, 2195, 1602, 1509, 1490, 1442, 1251, 1192, 1116, 1074 cm^{-1}. EI-MS: *m*/*z* (%) = 320 (52) $[M]^+$, 105 (100). $C_{18}H_{12}F_4O$ (320.29): calcd. C 67.50, H 3.78; found C 67.55, H 3.80.

(*E*)-4-(4-Chlorophenyl)-1,1,1-trifluoro-3-(2-phenylethynyl)but-3-en-2-ol (4e): White solid, 296 mg, 88% yield. M.p. 94–96 °C. ^{1}H NMR

(300 MHz, $CDCl_3$, 25 °C): δ = 7.87 (d, $^3J_{H,H}$ = 7.4 Hz, 2 H, Ar-H), 7.52–7.37 (m, 7 H, Ar-H), 6.92 (s, 1 H, =CH), 4.64 (m, 1 H, CF_3CH), 2.82 (d, $^3J_{H,H}$ = 8.4 Hz, 1 H, OH) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –77.5 (d, $^3J_{H,F}$ = 6.6 Hz, 3 F, CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 3468, 3086, 2194, 1589, 1490, 1442, 1252, 1194, 1096, 1012 cm^{-1}. EI-MS: *m*/*z* (%) = 336 (15) $[M]^+$, 105 (100). $C_{18}H_{12}ClF_3O$ (336.74): calcd. C 64.20, H 3.59; found C 64.30, H 3.52.

(*E*)-4-(4-Cyanophenyl)-1,1,1-trifluoro-3-(2-phenylethynyl)but-3-en-2-ol (4f): Yellow solid, 289 mg, 88% yield. M.p. 119–120 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.01 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H, Ar-H), 7.69 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H, Ar-H), 7.51–7.36 (m, 5 H, Ar-H), 7.01 (s, 1 H, =CH), 4.70 (m, 1 H, CF_3CH), 2.91 (d, $^3J_{H,H}$ = 8.1 Hz, 1 H, OH) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –77.3 (d, $^3J_{H,F}$ = 6.9 Hz, 3 F, CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 3385, 2237, 2198, 1601, 1489, 1338, 1261, 1168, 1139, 1124 cm^{-1}. EI-MS: *m*/*z* (%) = 327 (39) $[M]^+$, 105 (100). $C_{19}H_{12}F_3NO$ (327.31): calcd. C 69.72, H 3.70, N 4.28; found C 69.67, H 3.69, N 4.17.

(*E*)-1,1,1-Trifluoro-4-(4-nitrophenyl)-3-(2-phenylethynyl)but-3-en-2-ol (4g): Yellow solid, 326 mg, 94% yield. M.p. 147–149 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.93 (d, $^3J_{H,H}$ = 7.5 Hz, 2 H, Ar-H), 7.55–7.34 (m, 7 H, Ar-H), 6.96 (s, 1 H, =CH), 4.64 (m, 1 H, CF_3CH), 2.85 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H, OH) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –77.5 (d, $^3J_{H,F}$ = 6.9 Hz, 3 F, CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 3469, 2199, 1593, 1503, 1336, 1259, 1182, 1120 cm^{-1}. EI-MS: *m*/*z* (%) = 347 (17) $[M]^+$, 105 (100). $C_{18}H_{12}F_3NO_3$ (347.30): calcd. C 62.25, H 3.48, N 4.03; found C 62.13, H 3.63, N 3.81.

(*E*)-1,1,1-Trifluoro-4-(3-nitrophenyl)-3-(2-phenylethynyl)but-3-en-2-ol (4h): Yellow solid, 309 mg, 89% yield. M.p. 119–120 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 9.19 (t, $^3J_{H,H}$ = 2.1 Hz, 1 H, Ar-H), 8.21 (d, $^3J_{H,H}$ = 11.4 Hz, 1 H, Ar-H), 7.99 (d, $^3J_{H,H}$ = 11.4 Hz, 1 H, Ar-H), 7.62–7.38 (m, 6 H, Ar-H), 7.04 (s, 1 H, =CH), 4.71 (m, 1 H, CF_3CH), 2.85 (d, $^3J_{H,H}$ = 7.8 Hz, 1 H, OH) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –77.3 (d, $^3J_{H,F}$ = 7.5 Hz, 3 F, CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 3547, 2193, 1525, 1491, 1348, 1271, 1157, 1130, 1072 cm^{-1}. EI-MS: *m*/*z* (%) = 347 (1) $[M]^+$, 105 (100). $C_{18}H_{12}F_3NO_3$ (347.30): calcd. C 62.25, H 3.48, N 4.03; found C 62.31, H 3.62, N 3.91.

(*E*)-3-[2-(4-Chlorophenyl)ethynyl]-1,1,1-trifluoro-4-phenylbut-3-en-2-ol (4i): White solid, 296 mg, 88% yield. M.p. 71–73 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.88 (d, $^3J_{H,H}$ = 7.2 Hz, 2 H, Ar-H), 7.42–7.31 (m, 7 H, Ar-H), 6.97 (s, 1 H, =CH), 4.68 (m, 1 H, CF_3CH), 2.91 (d, $^3J_{H,H}$ = 8.1 Hz, 1 H, OH) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –77.4 (d, $^3J_{H,F}$ = 6.9 Hz, 3 F, CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 3449, 1490, 1334, 1255, 1176, 1128, 1089, 1014 cm^{-1}. EI-MS: *m*/*z* (%) = 336 (16) $[M]^+$, 139 (100). HRMS: calcd. for $C_{18}H_{12}ClF_3O$ 336.0529; found 336.0525.

(*E*)-3-[2-(4-Chlorophenyl)ethynyl]-1,1,1-trifluoro-4-(4-methylphenyl)-but-3-en-2-ol (4j): White solid, 305 mg, 87% yield. M.p. 81–83 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.80 (d, $^3J_{H,H}$ = 8.1 Hz, 2 H, Ar-H), 7.42 (d, $^3J_{H,H}$ = 6.3 Hz, 2 H, Ar-H), 7.34 (d, $^3J_{H,H}$ = 6.3 Hz, 2 H, Ar-H), 7.22 (d, $^3J_{H,H}$ = 8.1 Hz, 2 H, Ar-H), 6.94 (s, 1 H, =CH), 4.53 (m, 1 H, CF_3CH), 2.84 (d, $^3J_{H,H}$ = 6 Hz, 1 H, OH), 2.38 (s, 3 H, CH_3) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –77.5 (d, $^3J_{H,F}$ = 5.1 Hz, 3 F, CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 3467, 2924, 1603, 1580, 1490, 1254, 1173, 1125, 1013 cm^{-1}. EI-MS: *m*/*z* (%) = 350 (6) $[M]^+$, 139 (100). $C_{19}H_{14}ClF_3O$ (350.77): calcd. C 65.06, H 4.02; found C 65.03, H 4.03.

(*E*)-3-[2-(4-Chlorophenyl)ethynyl]-4-[4-(dimethylamino)phenyl]-1,1,1-trifluorobut-3-en-2-ol (4k): Orange solid, 304 mg, 80% yield. M.p. 124–126 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.84 (d, $^3J_{H,H}$ = 8.7 Hz, 2 H, Ar-H), 7.44 (d, $^3J_{H,H}$ = 8.7 Hz, 2 H, Ar-H), 7.34 (d, $^3J_{H,H}$ = 8.7 Hz, 2 H, Ar-H), 6.82 (d, $^3J_{H,H}$ = 8.7 Hz, 2 H, Ar-H), 7.03 (s, 1 H, =CH), 4.57 (m, 1 H, CF_3CH), 3.03 [s, 6 H, $N(CH_3)_2$], 2.71 (d, $^3J_{H,H}$ = 7.8 Hz, 1 H, OH) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –77.4 (d, $^3J_{H,F}$ = 6.0 Hz, 3 F, CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 3524, 2904, 2819, 2185, 1612, 1599, 1525, 1491, 1368, 1195, 1126, 1087 cm^{-1}. EI-MS: *m*/*z* (%) = 380 (5) $[M]^+$, 379 (20), 282 (8), 267 (8), 202 (5), 122 (8), 101 (6), 50 (7), 44 (100). $C_{20}H_{17}ClF_3NO$ (379.81): calcd. C 63.25, H 4.51, N 3.69; found C 63.73, H 4.55, N 3.47.

(*E*)-3-[2-(4-Chlorophenyl)ethynyl]-1,1,1-trifluoro-4-(4-fluorophenyl)-but-3-en-2-ol (4l): White solid, 294 mg, 83% yield. M.p. 83–84 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.91 (d, $^3J_{H,H}$ = 5.4 Hz, 1 H, Ar-H), 7.88 (d, $^3J_{H,H}$ = 5.4 Hz, 1 H, Ar-H), 7.42 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H, Ar-H), 7.35 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H, Ar-H), 7.09 (t, $^3J_{H,H}$ = 4.8 Hz, 2 H, Ar-H), 6.95 (s, 1 H, =CH), 4.64 (m, 1 H, CF_3CH), 2.77 (d, $^3J_{H,H}$ = 7.8 Hz, 1 H, OH) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –77.5 (d, $^3J_{H,F}$ = 6.9 Hz, 3 F, CF_3), –110.1 (m, 1 F) ppm. IR (KBr): $\tilde{\nu}$ = 3340, 2202, 1600, 1509, 1490, 1346, 1257, 1196, 1125, 1014 cm^{-1}. EI-MS: *m*/*z* (%) = 355 (13) $[M]^+$, 139 (100). $C_{18}H_{11}ClF_4O$ (354.73): calcd. C 60.95, H 3.13; found C 60.94, H 3.14.

(*E*)-3-[2-(4-Chlorophenyl)ethynyl]-4-(4-chlorophenyl)-1,1,1-trifluoro-but-3-en-2-ol (4m): White solid, 304 mg, 82% yield. M.p. 86–88 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.26 (d, $^3J_{H,H}$ = 8.7 Hz, 2 H, Ar-H), 8.04 (d, $^3J_{H,H}$ = 8.7 Hz, 2 H, Ar-H), 7.42 (d, $^3J_{H,H}$ = 8.7 Hz, 2 H), 7.37 (d, $^3J_{H,H}$ = 8.7 Hz, 2 H), 7.10 (s, 1 H, =CH), 4.75 (m, 1 H, CF_3CH), 3.06 (d, $^3J_{H,H}$ = 7.5 Hz, 1 H, OH) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –77.2 (d, $^3J_{H,F}$ = 5.1 Hz, 3 F, CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 3358, 1901, 1490, 1344, 1256, 1198, 1125, 1093, 1013 cm^{-1}. EI-MS: *m*/*z* (%) = 371 (56) $[M]^+$, 231 (100). $C_{18}H_{11}Cl_2F_3O$ (371.19): calcd. C 58.25, H 2.99; found C 58.05, H 3.17.

(*E*)-3-[2-(4-Chlorophenyl)ethynyl]-4-(4-cyanophenyl)-1,1,1-trifluoro-but-3-en-2-ol (4n): Yellow solid, 304 mg, 84% yield. M.p. 127–128 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.97 (d, $^3J_{H,H}$ = 8.1 Hz, 2 H, Ar-H), 7.69 (d, $^3J_{H,H}$ = 8.1 Hz, 2 H, Ar-H), 7.41 (d, $^3J_{H,H}$ = 8.7 Hz, 2 H, Ar-H), 7.37 (d, $^3J_{H,H}$ = 8.7 Hz, 2 H, Ar-H), 7.03 (s, 1 H, =CH), 4.71 (m, 1 H, CF_3CH), 2.90 (d, *J* = 7.8 Hz, 1 H, OH) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –77.3 (d, $^3J_{H,H}$ = 6.6 Hz, 3 F, CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 3364, 2241, 2199, 1601, 1589, 1490, 1344, 1259, 1182, 1124, 1013 cm^{-1}. EI-MS: *m*/*z* (%) = 362 (8) $[M]^+$, 44 (100). $C_{19}H_{11}ClF_3NO$ (361.75): calcd. C 63.08, H 3.06, N 3.87; found C 63.41, H 3.23, N 3.68.

(*E*)-3-[2-(4-Chlorophenyl)ethynyl]-1,1,1-trifluoro-4-(4-nitrophenyl)-but-3-en-2-ol (4o): Yellow solid, 324 mg, 85% yield. M.p. 128–129 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.27 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H, Ar-H), 8.04 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H, Ar-H), 7.43 (d, $^3J_{H,H}$ = 8.1 Hz, 2 H), 7.38 (d, $^3J_{H,H}$ = 8.1 Hz, 2 H, Ar-H), 7.10 (s, 1 H, =CH), 4.73 (m, 1 H, CF_3CH), 2.82 (d, *J* = 7.5 Hz, 1 H, OH) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –77.2 (d, $^3J_{H,F}$ = 6.9 Hz, 3 F, CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 3481, 2197, 1594, 1515, 1490, 1343, 1261, 1179, 1139, 1013 cm^{-1}. EI-MS: *m*/*z* (%) = 381 (21) $[M]^+$, 202 (100). $C_{18}H_{11}ClF_3NO_3$ (381.74): calcd. C 56.64, H 2.90, N 3.67; found C 56.83, H 3.09, N 3.50.

(*E*)-3-[2-(4-Chlorophenyl)ethynyl]-1,1,1-trifluoro-4-(3-nitrophenyl)-but-3-en-2-ol (4p): Yellow solid, 317 mg, 83% yield. M.p. 101–103 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 9.21 (t, $^3J_{H,H}$ = 2.1 Hz, 1 H, Ar-H), 8.22 (d, $^3J_{H,H}$ = 11.7 Hz, 1 H, Ar-H), 7.93 (d, $^3J_{H,H}$ = 8.1 Hz, 1 H, Ar-H), 7.61–7.36 (m, 5 H, Ar-H), 7.07 (s, 1 H, =CH), 4.71 (m, 1 H, CF_3CH), 2.85 (d, $^3J_{H,H}$ = 7.2 Hz, 1 H,

OH) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –77.3 (d, $^3J_{H,F}$ = 7.5 Hz, 3 F, CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 3529, 3114, 2196, 1651, 1590, 1527, 1492, 1351, 1270, 1160, 1074, 1012 cm^{-1}. EI-MS: *m/z* (%) = 381 (2) $[M]^+$, 139 (100). $C_{18}H_{11}ClF_3NO_3$ (381.74): calcd. C 56.64, H 2.90, N 3.67; found C 56.77, H 3.03, N 3.59.

General Procedure for Preparation of Substituted 2-(Trifluoromethyl)furans 5: A mixture of **4** (69.4 mg, 0.2 mmol), AgOTf (3 mg, 0.01 mmol, 5 mol-%) and 1,2-dichloroethane (2 mL) was stirred, protected from light, at 80 °C for the corresponding time mentioned in the text. The solution was evaporated under reduced pressure, and the residue was purified by flash chromatography on neutral aluminum oxide (hexane/EtOAc = 50:1 to 5:1) to afford pure **5**.

3-Benzyl-5-phenyl-2-(trifluoromethyl)furan (5a): Light yellow oil, 41 mg, 68% yield. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.64 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H, Ar-H), 7.37–7.24 (m, 8 H, Ar-H), 6.43 (s, 1 H, furan-H), 3.94 (s, 2 H, Ar*CH*$_2$) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –60.9 (s, 3 F, CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 3033, 2927, 2855, 1628, 1555, 1487, 1402, 1324, 1179, 1125, 1033 cm^{-1}. EI-MS: *m/z* (%) = 302 (100) $[M]^+$. $C_{18}H_{13}F_3O$ (302.30): calcd. C 71.52, H 4.33; found C 71.58, H 4.31.

3-(4-Methylbenzyl)-5-phenyl-2-(trifluoromethyl)furan (5b): Light yellow oil, 45 mg, 71% yield. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.55 (d, $^3J_{H,H}$ = 6.9 Hz, 2 H, Ar-H), 7.32–7.17 (m, 3 H, Ar-H), 7.05 (s, 4 H, Ar-H), 6.35 (s, 1 H, furan-H), 3.82 (s, 2 H, Ar*CH*$_2$), 2.25 (s, 3 H, Ar*CH*$_3$) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –60.9 (s, 3 F, CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 2926, 2859, 1629, 1516, 1487, 1401, 1325, 1178, 1056 cm^{-1}. EI-MS: *m/z* (%) = 316 (100) $[M]^+$. $C_{19}H_{15}F_3O$ (316.33): calcd. C 72.14, H 4.78; found C 72.07, H 4.98.

3-(4-Fluorobenzyl)-5-phenyl-2-(trifluoromethyl)furan (5d): Light yellow oil, 52 mg, 81% yield. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.57 (d, $^3J_{H,H}$ = 9.3 Hz, 2 H, Ar-H), 7.33–7.08 (m, 5 H, Ar-H), 6.93 (t, $^3J_{H,H}$ = 6.6 Hz, 2 H, Ar-H), 6.34 (s, 1 H, furan-H), 3.83 (s, 2 H, Ar*CH*$_2$) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –60.9 (s, 3 F, CF_3), –116.4 (m, 1 F) ppm. IR (KBr): $\tilde{\nu}$ = 3042, 1919, 1629, 1606, 1511, 1487, 1402, 1326, 1226, 1180, 1033 cm^{-1}. EI-MS: *m/z* (%) = 320 (20) $[M]^+$, 319 (100). $C_{18}H_{12}F_4O$ (320.29): calcd. C 67.50, H 3.78; found C 67.59, H 3.77.

3-(4-Chlorobenzyl)-5-phenyl-2-(trifluoromethyl)furan (5e): Light yellow oil, 33 mg, 49% yield. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.64 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H, Ar-H), 7.38–7.27 (m, 5 H, Ar-H), 7.15 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H, Ar-H), 6.41 (s, 1 H, furan-H), 3.91 (s, 2 H, Ar*CH*$_2$) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –61.0 (s, 3 F, CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 2926, 2854, 1630, 1492, 1401, 1324, 1179, 1127, 1034 cm^{-1}. EI-MS: *m/z* (%) = 336 (18) $[M]^+$, 335 (100). $C_{18}H_{12}ClF_3O$ (336.74): calcd. C 64.20, H 3.59; found C 64.32, H 3.68.

3-(4-Cyanobenzyl)-5-phenyl-2-(trifluoromethyl)furan (5f): Light yellow solid, 58 mg, 84% yield. M.p. 116–118 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.65 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H, Ar-H), 7.62 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H, Ar-H), 7.43–7.31 (m, 5 H, Ar-H), 6.42 (s, 1 H, furan-H), 4.01 (s, 2 H, Ar*CH*$_2$) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –61.0 (s, 3 F, CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 2995, 2224, 1608, 1553, 1488, 1401, 1331, 1307, 1177, 1148, 1106, 1035 cm^{-1}. EI-MS: *m/z* (%) = 327 (73) $[M]^+$, 44 (100). $C_{19}H_{12}F_3NO$ (327.31): calcd. C 69.72, H 3.70, N 4.28; found C 69.41, H 3.85, N 4.24.

3-(4-Nitrobenzyl)-5-phenyl-2-(trifluoromethyl)furan (5g): Light yellow solid, 63 mg, 91% yield. M.p. 76–78 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.19 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H, Ar-H), 7.66 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H, Ar-H), 7.40–7.26 (m, 5 H, Ar-H), 6.44 (s, 1 H, furan-H), 4.06 (s, 2 H, Ar*CH*$_2$) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –61.0 (s, 3 F, CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 3076, 2927, 2852, 1606, 1556, 1519, 1487, 1400, 1344, 1328, 1179, 1036 cm^{-1}. EI-MS: *m/z* (%) = 347 (100) $[M]^+$. $C_{18}H_{12}F_3NO_3$ (347.30): calcd. C 62.25, H 3.48, N 4.03; found C 62.13, H 3.38, N 3.91.

3-(3-Nitrobenzyl)-5-phenyl-2-(trifluoromethyl)furan (5h): Light yellow solid, 55 mg, 79% yield. M.p. 85–87 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.14–8.12 (m, 2 H, Ar-H), 7.66 (d, $^3J_{H,H}$ = 8.7 Hz, 2 H, Ar-H), 7.57–7.48 (m, 5 H, Ar-H), 6.46 (s, 1 H, furan-H), 4.06 (s, 2 H, Ar*CH*$_2$) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –61.0 (s, 3 F, CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 3126, 3088, 1630, 1555, 1520, 1489, 1403, 1355, 1180, 1038 cm^{-1}. EI-MS: *m/z* (%) = 347 (100) $[M]^+$. $C_{18}H_{12}F_3NO_3$ (347.30): calcd. C 62.25, H 3.48, N 4.03; found C 62.34, H 3.58, N 3.96.

3-Benzyl-5-(4-chlorophenyl)-2-(trifluoromethyl)furan (5i): Light yellow oil, 44 mg, 65% yield. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.55 (d, $^3J_{H,H}$ = 9.0 Hz, 2 H, Ar-H), 7.35–7.23 (m, 7 H, Ar-H), 6.41 (s, 1 H, furan-H), 3.93 (s, 2 H, Ar*CH*$_2$) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –60.9 (s, 3 F, CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 3032, 2927, 2855, 1604, 1483, 1418, 1323, 1180, 1032 cm^{-1}. EI-MS: *m/z* (%) = 336 (24) $[M]^+$, 335 (100). $C_{18}H_{12}ClF_3O$ (336.74): calcd. C 64.20, H 3.59; found C 64.07, H 3.61.

5-(4-Chlorophenyl)-3-(4-methylbenzyl)-2-(trifluoromethyl)furan (5j): Light yellow oil, 46 mg, 66% yield. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.56 (d, $^3J_{H,H}$ = 8.7 Hz, 2 H, Ar-H), 7.34 (d, $^3J_{H,H}$ = 8.7 Hz, 2 H, Ar-H), 7.12 (s, 4 H, Ar-H), 6.42 (s, 1 H, furan-H), 3.89 (s, 2 H, Ar*CH*$_2$), 2.33 (s, 3 H, Ar*CH*$_3$) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –61.0 (s, 3 F, CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 3047, 2927, 1627, 1514, 1483, 1418, 1392, 1324, 1179, 1033 cm^{-1}. EI-MS: *m/z* (%) = 350 (21) $[M]^+$, 349 (100). $C_{19}H_{14}ClF_3O$ (350.77): calcd. C 65.06, H 4.02; found C 65.13, H 4.05.

5-(4-Chlorophenyl)-3-(4-fluorobenzyl)-2-(trifluoromethyl)furan (5l): Light yellow oil, 50 mg, 71% yield. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.56 (d, $^3J_{H,H}$ = 8.7 Hz, 2 H, Ar-H), 7.34 (d, $^3J_{H,H}$ = 8.7 Hz, 2 H, Ar-H), 7.19 (d, $^3J_{H,H}$ = 5.7 Hz, 1 H, Ar-H), 7.16 (d, $^3J_{H,H}$ = 5.7 Hz, 1 H, Ar-H), 7.00 (t, *J* = 8.7 Hz, 2 H, Ar-H), 6.40 (s, 1 H, furan-H), 3.90 (s, 2 H, Ar*CH*$_2$) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –61.0 (s, 3 F, CF_3), –116.2 (m, 1 F) ppm. IR (KBr): $\tilde{\nu}$ = 2929, 2857, 1604, 1510, 1483, 1419, 1393, 1324, 1226, 1181, 1094, 1033 cm^{-1}. EI-MS: *m/z* (%) = 355 (19) $[M]^+$, 354 (100). $C_{18}H_{11}ClF_4O$ (354.73): calcd. C 60.95, H 3.13; found C 61.40, H 3.36.

3-(4-Chlorobenzyl)-5-(4-chlorophenyl)-2-(trifluoromethyl)furan (5m): Light yellow oil, 58 mg, 78% yield. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.56 (d, $^3J_{H,H}$ = 7.8 Hz, 2 H, Ar-H), 7.35 (d, $^3J_{H,H}$ = 7.5 Hz, 2 H, Ar-H), 7.29 (d, $^3J_{H,H}$ = 7.5 Hz, 2 H, Ar-H), 7.15 (d, $^3J_{H,H}$ = 7.8 Hz, 2 H, Ar-H), 6.39 (s, 1 H, furan-H), 3.90 (s, 2 H, Ar*CH*$_2$) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –61.1 (s, 3 F, CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 2928, 2856, 1725, 1629, 1604, 1483, 1324, 1182, 1054, 1016 cm^{-1}. EI-MS: *m/z* (%) = 371 (24) $[M]^+$, 57 (100). $C_{18}H_{11}Cl_2F_3O$ (371.19): calcd. C 58.25, H 2.99; found C 57.81, H 3.06.

5-(4-Chlorophenyl)-3-(4-cyanobenzyl)-2-(trifluoromethyl)furan (5n): Light yellow solid, 64 mg, 89% yield. M.p. 107–109 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.62 (d, $^3J_{H,H}$ = 8.7 Hz, 2 H, Ar-H), 7.58 (d, $^3J_{H,H}$ = 8.7 Hz, 2 H, Ar-H), 7.37 (d, $^3J_{H,H}$ = 8.7 Hz, 2 H, Ar-H), 7.33 (d, $^3J_{H,H}$ = 8.7 Hz, 2 H, Ar-H), 6.41 (s, 1 H, furan-H), 4.00 (s, 2 H, Ar*CH*$_2$) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –61.1 (s, 3 F, CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 2225, 1627, 1608, 1484, 1420, 1394, 1306, 1187, 1120, 1032 cm^{-1}. EI-MS: *m/z*

(%) = 362 (22) $[M]^+$, 361 (100). $C_{19}H_{11}ClF_3NO$ (361.75): calcd. C 63.08, H 3.06, N 3.87; found C 63.49, H 2.96, N 3.63.

5-(4-Chlorophenyl)-3-(4-nitrobenzyl)-2-(trifluoromethyl)furan (5o): Light yellow solid, 58 mg, 76% yield, M.p. 95–96 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.19 (d, $^3J_{H,H}$ = 8.7 Hz, 2 H, Ar-H), 7.59 (d, $^3J_{H,H}$ = 8.7 Hz, 2 H, Ar-H), 7.40 (d, $^3J_{H,H}$ = 4.5 Hz, 2 H, Ar-H), 7.37 (d, $^3J_{H,H}$ = 4.5 Hz, 2 H, Ar-H), 6.43 (s, 1 H, furan-H), 4.05 (s, 2 H, ArCH_2) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –61.1 (s, 3 F, CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 2961, 2859, 1729, 1605, 1521, 1483, 1423, 1340, 1286, 1180, 1037 cm^{-1}. EI-MS: *m*/*z* (%) = 382 (13) $[M]^+$, 149 (100). $C_{18}H_{11}ClF_3NO_3$ (381.74): calcd. C 56.64, H 2.90, N 3.67; found C 56.18, H 2.87, N 3.79.

5-(4-Chlorophenyl)-3-(3-nitrobenzyl)-2-(trifluoromethyl)furan (5p): Light yellow solid, 76 mg, >99% yield. M.p. 107–109 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.14 (s, 1 H, Ar-H), 8.11 (s, 1 H, Ar-H), 7.59 (d, $^3J_{H,H}$ = 8.7 Hz, 2 H, Ar-H), 7.54 (s, 1 H, Ar-H), 7.53 (s, 1 H, Ar-H), 7.38 (d, $^3J_{H,H}$ = 8.7 Hz, 2 H, Ar-H), 6.44 (s, 1 H, furan-H), 4.06 (s, 2 H, ArCH_2) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –61.0 (s, 3 F, CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 3118, 2936, 2867, 1629, 1520, 1482, 1356, 1331, 1186, 1058, 1035 cm^{-1}. EI-MS: *m*/*z* (%) = 382 (26) $[M]^+$, 381 (100). $C_{18}H_{11}ClF_3NO_3$ (381.74): calcd. C 56.64, H 2.90, N 3.67; found C 56.63, H 2.94, N 3.56.

Supporting Information (see also the footnote on the first page of this article): Spectroscopic data for literature-known compounds **1c**, **1d**, **1f**, **1g** and **1i**.

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