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Acid-promoted cyclization of 2,4-diaryl-1,1,1-trifluorobut-3-en-2-oles and their TMS-ethers into CF_3-indenes†

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2,4-Diaryl-1,1,1-trifluorobut-3-en-2-oles and their TMS-ethers in H_2SO_4 at room temperature in just 2 min are quantitatively cyclized into 1-aryl-3-trifluoromethyl-1*H*-indenes. The reaction proceeds through an intermediate formation of the corresponding CF_3-allyl cations, which are cyclized regioselectively at the allyl carbon atom most remote from the CF_3-group. The obtained CF_3-indenes in solution of EtOAc in the presence of silica gel at room temperature over 4 h are quantitatively isomerized into 3-aryl-1-trifluoromethyl-1*H*-indenes.

Introduction

Allyl alcohols are valuable synthons in organic chemistry. Recently we have shown[1–3] that reactions of some trifluoromethyl substituted allyl alcohols with arenes under the action of Brønsted or Lewis acids have resulted in the formation of trifluoromethylated alkenes, indanes, or indenes. Synthesis of indenes[4–6] is an actual goal in chemistry, biology, and medicine. For instance, indene derivatives are widely used as biologically active compounds,[7,8] and ligands for metallocomplexes.[9–12] Introduction of a trifluoromethyl group into the indene core may confer new chemical, biological (lipophilicity and bioavailability), and physical properties to the molecules, due to the strong electron acceptor characteristic of the CF_3 group. CF_3-indenes are rather rare compounds, and there are just a few reports on their synthesis.[13–17] For instance, Langlois *et al.* showed just one example of BF_3-promoted cyclization of CF_3-allyl alcohol into the corresponding CF_3-indene.[13]

The main goal of this work was a study of acid-promoted electrophilic transformation of 2,4-diaryl-1,1,1-trifluorobut-3-en-2-oles **2** and their TMS-ethers **1**. CF_3-TMS-ethers **1** are easily available from chalcones by trifluoromethylation of the carbonyl group with CF_3TMS followed by desilylation with $SnCl_2$ or aqueous HCl leading to CF_3-allyl alcohols **2** (Scheme 1).

Results and discussion

First, we decided to study plausible reaction cationic intermediates by means of quantum chemical calculations. One would expect that compounds **1**/**2** under the action of Brønsted or Lewis acids could give rise to the corresponding CF_3-allyl cations.[13] To estimate electronic characteristics of these cations we carried out DFT calculations of species **A** generated from **1a**/**2a** by the protonation of the OX group (X = TMS or H), followed by elimination of HOX (Fig. 1). The following parameters were calculated: E – energy of the HOMO and LUMO, global electrophilicity index ω,[18,19] natural charges q, contribution of the atomic orbital to the molecular orbital k. The calculation shows that carbon C^2 bears a large negative charge $-0.21e$, but carbon C^4 has a small positive charge and gives rather big contribution (19.6%) to the LUMO. These data demonstrate that the reactive electrophilic center of cation **A** should be carbon C^4 by both charge and orbital control. Species **A** possesses a big value of ω index 7.0 eV, pointing out its high electrophilicity.

Then we carried out reactions of the series of compounds **1**/**2** under the action of various acidic reagents (Table 1). Indeed, the cyclization of **1**/**2** into CF_3-indenes **3** takes place showing that carbon C^4 is a reactive center in the corresponding intermediate cations **A**. Among all other tested Brønsted and Lewis acids, sulfuric acid (H_2SO_4) was found to be one of the best for this transformation, and the reaction in this acid took just 2 min (Table 1). Alcohol **2a** was not converted into acetic acid (room temperature, 4 h), and remained unreacted. On the other hand, strong Lewis acids AlX_3 (X = Cl, Br) in the reaction with **2a** led to complex oligomeric mixtures. The same reaction in trifluoroacetic needed a longer time

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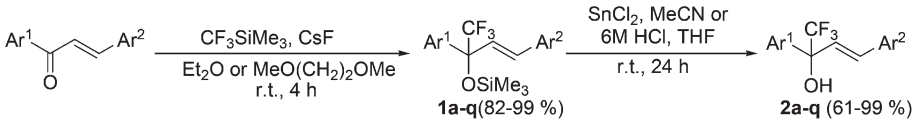


Scheme 1 Synthesis of CF_3-TMS-ethers **1** and the corresponding CF_3-alcohols **2** from chalcones (see substituents R^1, R^2 in aryl rings Ar^1, Ar^2, respectively, in Table 1).

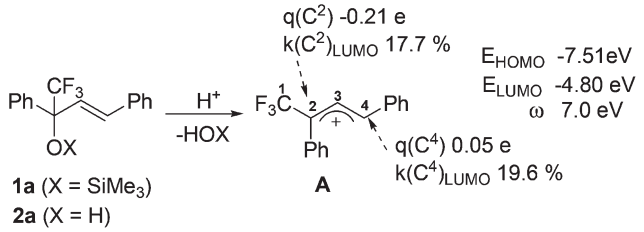


Fig. 1 Selected electronic characteristics (DFT calculations) of cation **A** generated from **1a**/**2a** by protonation of the OX group, followed by elimination of HOX (energy of the HOMO and LUMO *E*, global electrophilicity index $\omega = (E_{HOMO} + E_{LUMO})^2/8(E_{LUMO} - E_{HOMO})$, natural charges *q*, contribution of the atomic orbital to the molecular orbital *k*).

Table 1 Cyclization of compounds **1/2** in H_2SO_4 (50 equiv.) at room temperature for 2 min leading to CF_3-indenes **3**

	Starting compounds			Reaction products	
		R^1, R^2 in **1/2**, R^2 in **3**			
Entry	**1/2**	R^1	R^2	R^1	**3** [a] (yield, %)
1	**1a/2a**	H	H	H	**3a** (90)
2	**1b/2b**	4-Me	H	6-Me	**3b** (99)
3	**1c/2c**	H	4-Me	H	**3c** (99)
4	**1d/2d**	4-Me	4-Me	6-Me	**3d** (99)
5	**1e/2e**	4-MeO	H	6-MeO	**3e** (97) (97[b])
6	**1f/2f**	H	4-MeO	H	**3f** (97) (97[b])
7	**1g/2g**	3,4-Di(MeO)	H	5,6-Di(MeO)	**3g** (95) (98[b])
8	**1h/2h**	4-MeO	4-MeO	6-MeO	**3h** (10) (92[b])
9	**1i/2i**	4-Me	3,4-Di(MeO)	6-Me	**3i** (20) (50[b])
10[c]	**1j/2j**	3,4-Di(Me)	H	5,6-Di(Me)	**3j1** (53)
				6,7-Di(Me)	**3j2** (43)
11	**1k**	2,4-Di(Me)	H	4,6-Di(Me)	**3k** (97)
12	**1l**	2,5-Di(Me)	H	4,7-Di(Me)	**3l** (97)
13	**1m/2m**	2,4,6-Tri(Me)	H	4,6,7-Tri(Me)	**3m** (97)
14	**1n/2n**	H	3,4-OCH_2O	H	**3n** (68) (91[b])
15	**1o/2o**	H	4-Cl	H	**3o** (97)
16	**1p**	4-F	3,4-Di(Me)	6-F	**3p** (97)
17	**1q**	4-F	3,4-Di(MeO)	6-F	**3q** (74)[d]

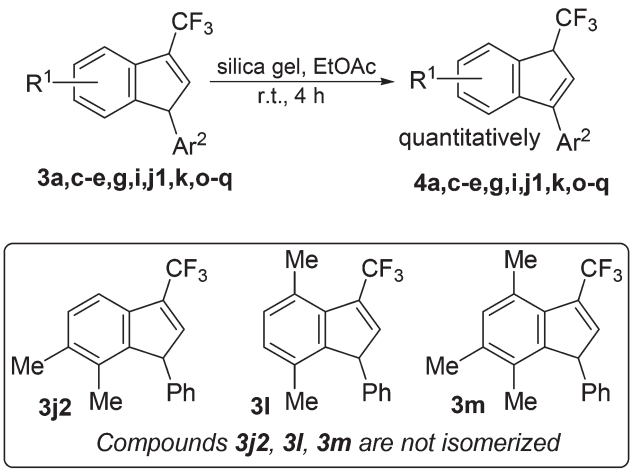
[a] Isolated yields. [b] Yield obtained with the reaction in CF_3CO_2H (50 equiv.), instead of H_2SO_4, for 5 min. [c] Two regioisomers **3j1** and **3j2** with a ratio 1.25 : 1 and 96% yield were obtained. [d] The mixture of isomeric indenes **3q** and **4q** in a ratio of 8 : 1, respectively, was obtained (see Scheme 2).

(room temperature, 1 h) and gave **3a** in 88% yield. Triflic acid CF_3SO_3H (TfOH) may be used as well; indene **3a** was formed in 2–3 min in 82% yield in this acid. However, we finally chose H_2SO_4 because it is a cheap and easy to handle reagent.

Both CF_3-TMS-ethers **1** and CF_3-allyl alcohols **2** gave the same indenes with the same high yields (Table 1). In most of the cases, the formation of indenes **3a–q** was quantitative (Table 1). However, in H_2SO_4 compounds **3h** and **3i** bearing donating methoxy groups were formed in low yields of 10 and 20%, respectively, due to the consequent transformations of these electron-rich indenes in H_2SO_4. The use of less acidic CF_3CO_2H resulted in much higher yields of **3h** and **3i**, 92 and 50%, respectively (entries 8 and 9).

It should be noted that starting compounds **1/2**, bearing both electron withdrawing and donating substituents R^1, R^2 in aryl rings Ar^1, Ar^2, respectively, led to the exclusive formation of indenes **3**, formed by the cyclization at carbon C^4 in CF_3-allyl cations **A** (see Fig. 1). The formation of alternative indene structures by cyclization at carbon C^2 in species **A** was not observed at all. This regioselectivity in reactions of CF_3-cations **A** is contrary to the non-selective behaviour of other allyl cations without the CF_3-substituent.[20]

Despite that indenes **3** were formed quantitatively without any further purification, under the attempt of their additional column chromatography isolation with silica gel, the isomerization into other indenes **4** was observed (Scheme 2). Thus, we developed the procedure for this quantitative isomerization by stirring a solution of compounds **3** in EtOAc in the presence of



Scheme 2 Isomerization of CF_3-indenes **3** into **4** (see substituents R^1, R^2 in aryl rings Ar^1, Ar^2, respectively, in Table 1).

silica gel at room temperature for 4 h (see Scheme 2 for selected indenes **3**/**4**). Compared with compounds **3**, their isomers **4** should be thermodynamically more stable, because of the additional conjugation of the indene $C^2{=}C^3$ double bond with the aryl group Ar^2. Some of the indenes **3** were isomerized very easily. Thus, under the isolation (without column chromatography with silica gel) of **3q**, the additional formation of the corresponding isomeric indene **4q** was observed (entry 17, Table 1). On the other hand, polymethylated indenes **3j2**, **3l** and **3m**, bearing a methyl group in the position 7 of the indene system, were not isomerized at all, presumably, because of the steric hindrance from this methyl substituent. Most likely, the presence of the substituent in the indene position 7 is a crucial point for this isomerization. Any bulky group in this position may disturb a flat orientation of ring Ar^2 relatively to the indene plane, which is thermodynamically favorable for conjugation of their π-systems. A shift of the double bond in the indene system with a formation of isomeric indenes has also been observed under the action of various basic or acidic reagents.[13,21–23]

Conclusion

We have found a novel, effective and simple method for the synthesis of two series of isomeric CF_3-indenes based on acid (H_2SO_4 or CF_3CO_2H)-promoted cyclization of 2,4-diaryl-1,1,1-trifluorobut-3-en-2-oles or their TMS-ethers.

Experimental part

Instruments

The NMR spectra of solutions of compounds in $CDCl_3$ were recorded on a Bruker AVANCE III 400 (at 400, 376 and 100 MHz for ^1H, ^{19}F and ^{13}C NMR spectra, respectively) spectrometer at 25 °C. The residual proton-solvent peak $CDCl_3$ (δ 7.26 ppm) for ^1H NMR spectra and the carbon signal of $CDCl_3$ (δ 77.0 ppm) for ^{13}C NMR spectra were used as references. ^{19}F NMR spectra were indirectly referred to the signal of $CFCl_3$ (δ 0.0 ppm). HRMS was carried out with a Bruker maXis HRMS-ESI-QTOF and a Varian 902-MS MALDI mass spectrometer. Chromato-mass-spectrometry data were obtained using a Shimadzu QP-2010 Ultra equipped with a SPB-1 SULFUR capillary column (30 m × 0.32 mm), the thickness of the stationary phase being 1.25 μm. The preparative reactions were monitored by thin-layer chromatography carried out on silica gel plates (Alugram SIL G/UV-254), using UV light for detection. Preparative TLC was performed on silica gel Chemapol L 5/40 with the petroleum ether–ethyl acetate mixture as an eluent.

DFT calculations

All computations were carried out at the DFT/HF hybrid level of theory using the Becke's three-parameter hybrid exchange functional in combination with the gradient-corrected correlation functional of Lee, Yang, and Parr (B3LYP) by using GAUSSIAN 2009 program packages.[24] The geometry optimization was performed using the 6-311+G(2d,2p) basis set (standard 6-311 basis set added with polarization (d, p) and diffuse functions). Optimizations were performed on all degrees of freedom, and solvent-phase optimized structures were verified as true minima with no imaginary frequencies. The Hessian matrix was calculated analytically for the optimized structures in order to prove the location of correct minima and to estimate the thermodynamic parameters. Gibbs free energies were calculated at 25 °C. Solvent-phase calculations used the Polarizable Continuum Model (PCM).

Synthesis and characterization of compounds 1 and 2

Trifluoromethylation of chalcones with CF_3SiMe_3 leading to compounds **1** was carried out according to the literature procedures.[25,26] Detrimethylsilylation of compounds **1** giving alcohols **2** was carried out with aqueous HCl[25] or with $SnCl_2$.[27]

Trimethylsilyl ether of (*E*)-1,1,1-trifluoro-2,4-diphenylbut-3-en-2-ol (1a). Yield 82%. Colorless solid. M.p. 49–50 °C (oil lit.[25,26]). ^1H NMR ($CDCl_3$, 400 MHz) δ, ppm: 0.16 s (9H, $SiMe_3$), 6.56 d (1H, =CH, J 16.3 Hz), 6.71 d (1H, =CH, J 16.3 Hz), 7.29–7.43 m ($8H_{arom.}$), 7.60–7.62 m ($2H_{arom.}$). ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: −77.40 s (CF_3). HRMS: $C_{19}H_{21}F_3OSiAg$ found 457.0360 $[M + Ag]^+$; calcd 457.0359.

Trimethylsilyl ether of (*E*)-1,1,1-trifluoro-2-(4-methylphenyl)-4-phenylbut-3-en-2-ol (1b). Yield 96%. Yellow oil. ^1H NMR ($CDCl_3$, 400 MHz) δ, ppm: 0.15 s (9H, $SiMe_3$), 2.39 s (3H, Me), 6.56 d (1H, =CH, J 16.3 Hz), 6.72 d (1H, =CH, J 16.3 Hz), 7.21 d ($2H_{arom.}$, J 8.1 Hz), 7.29–7.43 m ($5H_{arom.}$), 7.49 d ($2H_{arom.}$, J 8.1 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 2.2 ($SiMe_3$), 21.2 (Me), 80.0 q (C^2, $J_{C–F}$ 28.8 Hz), 125.2 q (CF_3, $J_{C–F}$ 286.8 Hz), 127.0, 127.2, 128.0, 128.7, 128.8, 128.9, 135.2, 135.2, 135.9, 138.5. ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: −77.57 s (CF_3). HRMS: $C_{20}H_{23}F_3OSiAg$ found 471.0517 $[M + Ag]^+$; calcd 471.0516.

Trimethylsilyl ether of (*E*)-1,1,1-trifluoro-4-(4-methylphenyl)-2-phenylbut-3-en-2-ol (1c). Yield 92%. Yellow oil. ^1H NMR ($CDCl_3$, 400 MHz) δ, ppm: 0.16 s (9H, $SiMe_3$), 2.37 s (3H, Me), 6.52 d (1H, =CH, J 16.4 Hz), 6.66 d (1H, =CH, J 16.4 Hz), 7.17 d ($2H_{arom.}$, J 8.0 Hz), 7.31 d ($2H_{arom.}$, J 8.0 Hz), 7.36–7.43 m ($3H_{arom.}$), 7.60–7.62 m ($2H_{arom.}$). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 2.2 ($SiMe_3$), 21.4 (Me), 80.1 q (C^2, $J_{C–F}$ 28.8 Hz), 125.2 q (CF_3, $J_{C–F}$ 286.6 Hz), 126.0, 126.9, 128.0, 128.1, 128.6, 129.7, 133.1, 135.4, 138.2, 138.8. ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: −77.57 s (CF_3). HRMS: $C_{20}H_{23}F_3OSiAg$ found 471.0507 $[M + Ag]^+$; calcd 471.0516.

Trimethylsilyl ether of (*E*)-1,1,1-trifluoro-2,4-bis(4-methylphenyl)but-3-en-2-ol (1d). Yield 99%. Yellow oil. ^1H NMR ($CDCl_3$, 400 MHz) δ, ppm: 0.15 s (9H, $SiMe_3$), 2.36 s (3H, Me), 2.39 s (3H, Me), 6.51 d (1H, =CH, J 16.3 Hz), 6.67 d (1H, =CH, J 16.3 Hz), 7.17 d ($2H_{arom.}$, J 8.0 Hz), 7.20 d ($2H_{arom.}$, J 8.1 Hz), 7.31 d ($2H_{arom.}$, J 8.0 Hz), 7.49 d ($2H_{arom.}$, J 8.1 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 2.2 ($SiMe_3$), 21.2 (Me), 21.4 (Me), 80.0 q (C^2, $J_{C–F}$ 28.7 Hz), 125.2 q (CF_3, $J_{C–F}$ 286.6 Hz), 126.1, 126.9, 128.1, 128.8, 129.6, 133.2, 135.2,

135.3, 138.4, 138.7. ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: −77.75 c (CF_3). HRMS: $C_{21}H_{25}F_3OSiAg$ found 485.0668 $[M + Ag]^+$; calcd 485.0672.

Trimethylsilyl ether of (*E*)-1,1,1-trifluoro-2-(4-methoxyphenyl)-4-phenylbut-3-en-2-ol (1e). Yield 98%. Yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 0.18 s (9H, $SiMe_3$), 3.83 s (3H, OMe), 6.46 d (1H, =CH, *J* 16.3 Hz), 6.64 d (1H, =CH, *J* 16.3 Hz), 6.91 d ($2H_{arom.}$, *J* 8.7 Hz), 7.37 d ($2H_{arom.}$, *J* 8.7 Hz), 7.40–7.42 m ($3H_{arom.}$), 7.63–7.65 m ($2H_{arom.}$). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 2.2 ($SiMe_3$), 55.4 (OMe), 80.2 q (C^2, *J* 28.8 Hz), 114.4, 124.7, 125.2 q (CF_3, *J* 286.5 Hz), 128.0, 128.2, 128.3, 128.6, 128.6, 135.1, 138.3, 160.2. ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: −77.64 c (CF_3). HRMS: $C_{20}H_{23}F_3O_2SiAg$ found 487.0469 $[M + Ag]^+$; calcd 487.0465.

Trimethylsilyl ether of (*E*)-1,1,1-trifluoro-4-(4-methoxyphenyl)-2-phenylbut-3-en-2-ol (1f). Yield 99%. Yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 0.15 s (9H, $SiMe_3$), 3.85 s (3H, OMe), 6.56 d (1H, =CH, *J* 16.3 Hz), 6.73 d (1H, =CH, *J* 16.3 Hz), 6.93 d ($2H_{arom.}$, *J* 8.6 Hz), 7.30–7.37 m ($3H_{arom.}$), 7.42–7.44 m ($2H_{arom.}$), 7.53 d ($2H_{arom.}$, *J* 8.6 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 2.2 ($SiMe_3$), 55.4 (OMe), 79.8 q (C^2, J_{C-F} 28.9 Hz), 113.4, 125.2 q (CF_3, J_{C-F} 286.5 Hz), 127.0, 127.2, 128.7, 128.9, 129.5, 130.0, 135.2, 135.9, 159.9. ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: −77.73 c (CF_3). HRMS: $C_{20}H_{23}F_3O_2SiAg$ found 487.0477 $[M + Ag]^+$; calcd 487.0465.

Trimethylsilyl ether of (*E*)-1,1,1-trifluoro-2-(3,4-dimethoxyphenyl)-2-phenylbut-3-en-2-ol (1g). Yield 99%. Yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 0.15 s (9H, $SiMe_3$), 3.88 s (3H, OMe), 3.91 s (3H, OMe), 6.55 d (1H, =CH, *J* 16.3 Hz), 6.71 d (1H, =CH, *J* 16.3 Hz), 6.88 d ($1H_{arom.}$, *J* 9.0 Hz), 7.14–7.15 m ($2H_{arom.}$), 7.26–7.43 m ($5H_{arom.}$). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 2.2 s ($SiMe_3$), 56.0 (OMe), 56.0 (OMe), 79.9 q (C^2, J_{C-F} 28.7 Hz), 110.5, 111.6, 120.8, 125.2 q (CF_3, J_{C-F} 287.0 Hz), 127.0, 127.0, 128.8, 129.0, 130.4, 135.4, 135.9, 148.5, 149.3. ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: −77.64 c (CF_3). HRMS: $C_{21}H_{25}F_3O_2SiAg$ found 517.0559 $[M + Ag]^+$; calcd 517.0571.

Trimethylsilyl ether of (*E*)-1,1,1-trifluoro-2,4-bis(4-methoxyphenyl)but-3-en-2-ol (1h). Yield 95%. Yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 0.14 s (9H, $SiMe_3$), 3.82 s (3H, OMe), 3.84 s (3H, OMe), 6.41 d (1H, =CH, *J* 16.3 Hz), 6.62 d (1H, =CH, *J* 16.3 Hz), 6.89 d ($2H_{arom.}$, *J* 8.7 Hz), 6.92 d ($2H_{arom.}$, *J* 8.8 Hz), 7.35 d ($2H_{arom.}$, *J* 8.7 Hz), 7.52 d ($2H_{arom.}$, *J* 8.8 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 2.2 ($SiMe_3$), 55.4 (OMe), 55.5 (OMe), 79.9 q (C^2, J_{C-F} 29.0 Hz), 113.4, 114.4, 124.9, 125.3 q (CF_3, J_{C-F} 286.6 Hz), 128.3, 128.6, 129.5, 130.2, 134.9, 159.8, 160.2. ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: −78.02 c (CF_3). HRMS: $C_{21}H_{25}F_3O_2SiAg$ found 517.0550 $[M + Ag]^+$; calcd 517.0571.

Trimethylsilyl ether of (*E*)-1,1,1-trifluoro-2-(4-methylphenyl)-4-(3,4-dimethoxyphenyl)but-3-en-2-ol (1i). Yield 99%. Yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 0.14 s (9H, $SiMe_3$), 2.39 s (3H, Me), 3.89 s (3H, OMe), 3.91 s (3H, OMe), 6.40 d (1H, =CH, *J* 16.3 Hz), 6.61 d (1H, =CH, *J* 16.3 Hz), 6.85 d ($1H_{arom.}$, *J* 8.3 Hz), 6.93 d ($1H_{arom.}$, *J* 1.9 Hz), 6.96 dd ($1H_{arom.}$, *J* 8.3 Hz, *J* 1.9 Hz), 7.21 d ($2H_{arom.}$, *J* 8.1 Hz), 7.49 d ($2H_{arom.}$, *J* 8.1 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 2.2 ($SiMe_3$), 21.2 (Me), 56.1 (OMe), 56.1 (OMe), 80.1 q (C^2, *J* 28.8 Hz), 104.4, 109.4, 111.4, 120.3, 125.1, 125.2 q (CF_3, J_{C-F} 286.5 Hz), 128.1, 128.8, 128.9, 135.1, 135.2, 138.4, 149.4, 149.8. ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: −77.68 (CF_3). HRMS: $C_{22}H_{27}F_3O_3SiAg$ found 531.0727 $[M + Ag]^+$; calcd 531.0731.

Trimethylsilyl ether of (*E*)-1,1,1-trifluoro-2-(3,4-dimethylphenyl)-2-phenylbut-3-en-2-ol (1j). Yield 93%. Yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 0.15 s (9H, $SiMe_3$), 2.30 s (6H, 2Me), 6.55 d (1H, =CH, *J* 16.3 Hz), 6.73 d (1H, =CH, *J* 16.3 Hz), 7.16 d ($1H_{arom.}$, *J* 7.8 Hz), 7.29–7.39 m ($5H_{arom.}$), 7.42–7.44 m ($2H_{arom.}$). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 2.2 ($SiMe_3$), 19.6 (Me), 20.2 (Me), 80.0 q (C^2, J_{C-F} 28.8 Hz), 125.2 q (CF_3, J_{C-F} 286.7 Hz), 125.5, 127.0, 127.3, 128.7, 128.9, 129.2, 129.4, 135.0, 135.5, 136.0, 136.2, 137.1. ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: −77.41 c (CF_3). HRMS: $C_{21}H_{25}F_3OSiAg$ found 485.0668 $[M + Ag]^+$; calcd 485.0672.

Trimethylsilyl ether of (*E*)-1,1,1-trifluoro-2-(2,4-dimethylphenyl)-2-phenylbut-3-en-2-ol (1k). Yield 94%. Yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 0.09 s (9H, $SiMe_3$), 2.33 s (3H, Me), 2.39 s (3H, Me), 6.47 d (1H, =CH, *J* 16.4 Hz), 6.67 d (1H, =CH, *J* 16.4 Hz), 7.01–7.03 m ($2H_{arom.}$), 7.27–7.42 m ($5H_{arom.}$), 7.50 d ($1H_{arom.}$, *J* 7.7 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 1.8 ($SiMe_3$), 21.0 (Me), 22.6 (Me), 81.0 q (C^2, J_{C-F} 28.5 Hz), 125.6 q (CF_3, J_{C-F} 287.4 Hz), 126.2, 126.9, 128.3, 128.5, 128.9, 133.7, 133.8, 134.1, 136.2, 138.0, 138.3. ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: −74.50 c (CF_3). HRMS: $C_{21}H_{25}F_3OSiAg$ found 485.0664 $[M + Ag]^+$; calcd 485.0672.

Trimethylsilyl ether of (*E*)-1,1,1-trifluoro-2-(2,5-dimethylphenyl)-2-phenylbut-3-en-2-ol (1l). Yield 97%. Yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 0.09 s (9H, $SiMe_3$), 2.36 s (3H, Me), 2.38 s (3H, Me), 6.47 d (1H, =CH, *J* 16.4 Hz), 6.68 d (1H, =CH, *J* 16.4 Hz), 7.08 m ($2H_{arom.}$), 7.28–7.37 m ($3H_{arom.}$), 7.40–7.42 m ($3H_{arom.}$). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 1.7 ($SiMe_3$), 21.3 (Me), 22.2 (Me), 81.0 q (C^2, J_{C-F} 28.6 Hz), 125.5 q (CF_3, J_{C-F} 287.6 Hz), 126.8, 128.1, 128.4, 128.8, 129.0, 129.2, 132.8, 134.1, 134.7, 134.9, 136.1, 136.2. ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: −74.24 c (CF_3). HRMS: $C_{21}H_{25}F_3OSiAg$ found 485.0662 $[M + Ag]^+$; calcd 485.0672.

Trimethylsilyl ether of (*E*)-1,1,1-trifluoro-2-(2,4,6-trimethylphenyl)-2-phenylbut-3-en-2-ol (1m). Yield 99%. Yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 0.10 s (9H, $SiMe_3$), 2.25 s (3H, Me), 2.27 s (3H, Me), 2.36 s (3H, Me), 6.48 d (1H, =CH, *J* 16.4 Hz), 6.69 d (1H, =CH, *J* 16.4 Hz), 6.97 s ($1H_{arom.}$), 7.27–7.43 m ($6H_{arom.}$). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 1.7 ($SiMe_3$), 19.2 (Me), 19.5 (Me), 22.0 (Me), 80.8 q (C^2, J_{C-F} 28.5 Hz), 125.4 q (CF_3, J_{C-F} 287.6 Hz), 126.7, 128.2, 128.3, 128.7, 129.6, 133.2, 133.6, 133.9, 134.2, 135.1, 136.1, 136.7. ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: −74.54 c (CF_3). HRMS: $C_{22}H_{27}F_3OSiAg$ found 499.0834 $[M + Ag]^+$; calcd 499.0829.

Trimethylsilyl ether of (*E*)-1,1,1-trifluoro-4-(3,4-methylenedioxyphenyl)-2-phenylbut-3-en-2-ol (1n). Yield 99%. Yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 0.16 s (9H, $SiMe_3$), 5.98 s (2H, CH_2), 6.39 d (1H, =CH, *J* 16.2 Hz), 6.59 d (1H, =CH, *J* 16.2 Hz), 6.78 d ($1H_{arom.}$, *J* 8.0 Hz), 6.83 d ($1H_{arom.}$, *J* 8.0 Hz), 6.96 s ($1H_{arom.}$), 7.36–7.42 m ($3H_{arom.}$), 7.59–7.61 m ($2H_{arom.}$). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 2.2 ($SiMe_3$), 80.1 q (C^2, J_{C-F}

28.8 Hz), 101.4, 105.9, 108.6, 122.2, 125.2 q (CF_3, $J_{C–F}$ 286.3 Hz), 125.2, 128.0, 128.1, 128.6, 130.3, 135.2, 138.2, 148.3, 148.5. ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: −77.59 c (CF_3). HRMS: $C_{20}H_{21}F_3O_3SiAg$ found 501.0252 $[M + Ag]^+$; calcd 501.0258.

Trimethylsilyl ether of (*E*)-1,1,1-trifluoro-4-(4-chlorophenyl)-2-phenylbut-3-en-2-ol (1o). Yield 99%. Yellow oil. ^1H NMR ($CDCl_3$, 400 MHz) δ, ppm: 0.15 s (9H, $SiMe_3$), 6.53 d (1H, =CH, *J* 16.3 Hz), 6.67 d (1H, =CH, *J* 16.3 Hz), 7.34 s ($4H_{arom.}$), 7.38–7.43 m ($3H_{arom.}$), 7.59–7.61 m ($2H_{arom.}$). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 2.1 ($SiMe_3$), 80.1 q (C^2, $J_{C–F}$ 29.0 Hz), 125.1 q (CF_3, $J_{C–F}$ 286.8 Hz), 127.9, 128.0, 128.2, 128.2, 128.8, 129.2, 133.9, 134.4, 134.6, 138.0. ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: −77.19 c (CF_3). HRMS: $C_{21}H_{25}F_3{}^{35}ClOSiAg$ found 490.9965 $[M + Ag]^+$; calcd 490.9969.

Trimethylsilyl ether of (*E*)-1,1,1-trifluoro-2-(4-fluorophenyl)-4-(3,4-dimethylphenyl)but-3-en-2-ol (1p). Yield 96%. Yellow oil. ^1H NMR ($CDCl_3$, 400 MHz) δ, ppm: 0.17 s (9H, $SiMe_3$), 2.28 s (6H, 2Me), 6.50 d (1H, =CH, *J* 16.4 Hz), 6.61 d (1H, =CH, *J* 16.4 Hz), 7.05–7.18 m ($5H_{arom.}$), 7.59 dd ($2H_{arom.}$, *J* 8.6 Hz, *J* 5.5 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 2.1 ($SiMe_3$), 19.6 (Me), 19.8 (Me), 79.8 q (C^2, $J_{C–F}$ 29.0 Hz), 114.8 d ($J_{C–F}$ 21.5 Hz), 124.3, 125.1 q (CF_3, $J_{C–F}$ 286.6 Hz), 125.3, 128.3, 130.1 d (*J* 8.2 Hz), 130.2, 133.2, 134.1 d ($J_{C–F}$ 3.1 Hz), 135.9, 137.2, 137.7, 162.9 d ($J_{C–F}$ 247.6 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: −113.96 c ($1F_{arom.}$), −77.95 c (CF_3). HRMS: $C_{21}H_{24}F_4OSiAg$ found 503.0570 $[M + Ag]^+$; calcd 503.0578.

Trimethylsilyl ether of (*E*)-1,1,1-trifluoro-2-(4-fluorophenyl)-4-(3,4-dimethoxyphenyl)but-3-en-2-ol (1q). Yield 93%. Yellow oil. ^1H NMR ($CDCl_3$, 400 MHz) δ, ppm: 0.16 s (9H, $SiMe_3$), 3.90 s (3H, OMe), 3.91 s (3H, OMe), 6.39 d (1H, =CH, *J* 16.3 Hz), 6.57 d (1H, =CH, *J* 16.3 Hz), 6.85 d ($1H_{arom.}$, *J* 8.3 Hz), 6.92 d ($1H_{arom.}$, *J* 1.9 Hz), 6.96 dd ($1H_{arom.}$, *J* 8.3 Hz, *J* 1.9 Hz), 7.05–7.11 m ($2H_{arom.}$), 7.58 dd ($2H_{arom.}$, *J* 8.6 Hz, *J* 5.4 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 2.1 s ($SiMe_3$), 56.1 (OMe), 56.1 (OMe), 79.8 q (C^2, $J_{C–F}$ 29.0 Hz), 109.3, 111.4, 114.9 d ($J_{C–F}$ 21.5 Hz), 120.4, 124.6, 125.1 q (CF_3, $J_{C–F}$ 286.3 Hz), 128.6, 130.1 d ($J_{C–F}$ 8.3 Hz), 134.0 d ($J_{C–F}$ 3.2 Hz), 135.6, 149.4, 150.0, 163.0 d ($J_{C–F}$ 247.7 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: −113.88 c ($1F_{arom.}$), −77.90 c (CF_3). HRMS: $C_{21}H_{24}F_4O_3SiAg$ found 535.0484 $[M + Ag]^+$; calcd 535.0476.

(*E*)-1,1,1-Trifluoro-2,4-diphenylbut-3-en-2-ol (2a). Yield 95%. Yellow oil (oil lit.[24]). ^1H NMR ($CDCl_3$, 400 MHz) δ, ppm: 2.69 s (1H, OH), 6.73 d (1H, =CH, *J* 16.1 Hz), 6.89 d (1H, =CH, *J* 16.1 Hz), 7.28–7.45 m ($8H_{arom.}$), 7.65–7.67 m ($2H_{arom.}$). ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: −78.50 c (CF_3). HRMS: $C_{16}H_{13}F_3OAg$ found 384.9957 $[M + Ag]^+$; calcd 384.9964.

(*E*)-1,1,1-Trifluoro-2-(4-methylphenyl)-4-phenylbut-3-en-2-ol (2b). Yield 94%. Yellow solid. M.p. 53–55 °C. ^1H NMR ($CDCl_3$, 400 MHz) δ, ppm: 2.38 s (3H, Me), 2.66 s (1H, OH), 6.72 d (1H, =CH, *J* 16.1 Hz), 6.89 d (1H, =CH, *J* 16.1 Hz), 7.23 d ($2H_{arom.}$, *J* 8.1 Hz), 7.28–7.38 m ($3H_{arom.}$), 7.43–7.45 m ($2H_{arom.}$), 7.54 d ($2H_{arom.}$, *J* 8.1 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 21.21 (Me), 77.4 q (C^2, $J_{C–F}$ 29.0 Hz), 125.2 q (CF_3, $J_{C–F}$ 286.0 Hz), 126.7, 126.9, 126.9, 127.1, 128.7, 128.9, 129.2, 133.5, 134.6, 135.7, 138.9. ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: −78.57 c (CF_3). HRMS: $C_{17}H_{15}F_3OAg$ found 399.0124 $[M + Ag]^+$; calcd 399.0120.

(*E*)-1,1,1-Trifluoro-4-(4-methylphenyl)-2-phenylbut-3-en-2-ol (2c). Yield 92%. Yellow solid. M.p. 64–66 °C. ^1H NMR ($CDCl_3$, 400 MHz) δ, ppm: 2.36 s (3H, Me), 2.67 s (1H, OH), 6.68 d (1H, =CH, *J* 16.1 Hz), 6.85 d (1H, =CH, *J* 16.1 Hz), 7.16 d ($2H_{arom.}$, *J* 8.0 Hz), 7.33 d ($2H_{arom.}$, *J* 8.0 Hz), 7.37–7.44 m ($3H_{arom.}$), 7.65–7.67 m ($2H_{arom.}$). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 21.4 (Me), 77.5 q (C^2, $J_{C–F}$ 29.0 Hz), 125.2 q (CF_3, $J_{C–F}$ 286.0 Hz), 125.6, 127.0, 127.0, 128.5, 128.9, 129.6, 132.9, 133.6, 137.6, 138.8. ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: −78.55 c (CF_3). HRMS: $C_{17}H_{15}F_3OAg$ found 399.0110 $[M + Ag]^+$; calcd 399.0120.

(*E*)-1,1,1-Trifluoro-2,4-bis(4-methylphenyl)but-3-en-2-ol (2d). Yield 80%. Yellow solid. M.p. 49–51 °C. ^1H NMR ($CDCl_3$, 400 MHz) δ, ppm: 2.36 s (3H, Me), 2.38 s (3H, Me), 2.58 s (1H, OH), 6.66 d (1H, =CH, *J* 16.1 Hz), 6.84 d (1H, =CH, *J* 16.1 Hz), 7.16 d ($2H_{arom.}$, *J* 8.0 Hz), 7.22 d ($2H_{arom.}$, *J* 8.1 Hz), 7.32 d ($2H_{arom.}$, *J* 8.0 Hz), 7.53 d ($2H_{arom.}$, *J* 8.1 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 21.2 (Me), 21.4 (Me), 77.4 q (C^2, $J_{C–F}$ 28.6 Hz), 125.3 q (CF_3, *J* 286.2 Hz), 125.7, 126.9, 127.0, 129.2, 129.6, 132.9, 133.5, 134.7, 138.7, 138.8. ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: −78.65 c (CF_3). HRMS: $C_{18}H_{17}F_3OAg$ found 413.0267 $[M + Ag]^+$; calcd 413.0277.

(*E*)-1,1,1-Trifluoro-2-(4-methoxyphenyl)-4-phenylbut-3-en-2-ol (2e). Yield 94%. Yellow oil. ^1H NMR ($CDCl_3$, 400 MHz) δ, ppm: 2.69 s (1H, OH), 3.82 s (3H, OCH_3), 6.59 d (1H, =CH, *J* 16.1 Hz), 6.81 d (1H, =CH, *J* 16.1 Hz), 6.88 d ($2H_{arom.}$, *J* 8.8 Hz), 7.35–7.44 m ($5H_{arom.}$), 7.64–7.66 m ($2H_{arom.}$). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 55.5 (OMe), 77.5 q (C^2, $J_{C–F}$ 28.6 Hz), 114.3, 124.4, 125.3 q (CF_3, *J* 285.9 Hz), 127.0, 128.4, 128.4, 128.5, 128.9, 133.3, 137.7, 160.2. ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: −78.57 c (CF_3). HRMS: $C_{17}H_{15}F_3O_2Ag$ found 415.0089 $[M + Ag]^+$; calcd 415.0070.

(*E*)-1,1,1-Trifluoro-4-(4-methoxylphenyl)-2-phenylbut-3-en-2-ol (2f). Yield 61%. Yellow oil. ^1H NMR ($CDCl_3$, 400 MHz) δ, ppm: 2.66 s (1H, OH), 3.82 s (3H, OMe), 6.58 d (1H, =CH, *J* 16.1 Hz), 6.80 d (1H, =CH, *J* 16.1 Hz), 6.87 d ($2H_{arom.}$, *J* 8.8 Hz), 7.35–7.43 m ($5H_{arom.}$), 7.64–7.65 m ($2H_{arom.}$). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 55.5 (OMe), 77.5 q (C^2, $J_{C–F}$ 28.9 Hz), 114.3, 124.4, 125.3 q (CF_3, $J_{C–F}$ 286.1 Hz), 127.0, 128.3, 128.4, 128.4, 128.8, 133.3, 137.8, 160.1. ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: −78.59 c (CF_3). HRMS: $C_{17}H_{15}F_3O_2Ag$ found 415.0073 $[M + Ag]^+$; calcd 415.0070.

(*E*)-1,1,1-Trifluoro-2-(3,4-dimethoxyphenyl)-2-phenylbut-3-en-2-ol (2g). Yield 93%. Yellow oil. ^1H NMR ($CDCl_3$, 400 MHz) δ, ppm: 2.76 s (1H, OH), 3.89 s (3H, OMe), 3.90 s (3H, OMe), 6.69 d (1H, =CH, *J* 16.1 Hz), 6.88 d (1H, =CH, *J* 16.1 Hz), 6.88 d ($1H_{arom.}$, *J* 8.5 Hz), 7.16 d ($1H_{arom.}$, *J* 8.5 Hz), 7.19 s ($1H_{arom.}$), 7.28–7.37 m ($3H_{arom.}$), 7.43 m ($2H_{arom.}$). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 56.0 (OMe), 56.1 (OMe), 77.5 q (C^2, *J* 28.6 Hz), 110.3, 110.8, 119.8, 125.3 q (CF_3, $J_{C–F}$ 286.1 Hz), 126.7, 127.0, 128.8, 128.9, 129.9, 133.7, 135.7, 148.9, 149.5. ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: −78.54 c (CF_3). HRMS: $C_{18}H_{17}F_3O_3Ag$ found 445.0178 $[M + Ag]^+$; calcd 445.0175.

(*E*)-1,1,1-Trifluoro-2,4-bis(4-methoxyphenyl)but-3-en-2-ol (2h). Yield 99%. Yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 2.73 s (1H, OH), 3.81 s (3H, OMe), 3.82 s (3H, OMe), 6.56 d (1H, =CH, *J* 16.1 Hz), 6.79 d (1H, =CH, *J* 16.1 Hz), 6.87 d (2H$_{arom.}$, *J* 8.7 Hz), 6.92 d (2H$_{arom.}$, *J* 8.8 Hz), 7.36 d (2H$_{arom.}$, *J* 8.7 Hz), 7.56 d (2H$_{arom.}$, *J* 8.8 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 55.4 (OMe), 55.5 (OMe), 77.2 q (C^2, J_{C-F} 28.6 Hz), 113.8, 114.3, 124.5, 125.3 q (CF_3, J_{C-F} 286.0 Hz), 128.3, 128.5, 129.8, 133.1, 159.9, 160.1. ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: −78.77 c (CF_3). HRMS: $C_{18}H_{17}F_3O_3Ag$ found 445.0173 $[M + Ag]^+$; calcd 445.0175.

(*E*)-1,1,1-Trifluoro-2-(4-methylphenyl)-4-(3,4-dimethoxyphenyl) but-3-en-2-ol (2i). Yield 95%. Yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 2.37 s (3H, Me), 2.71 s (1H, OH), 3.88 s (3H, OMe), 3.90 s (3H, OMe), 6.55 d (1H, =CH, *J* 16.0 Hz), 6.79 d (1H, =CH, *J* 16.0 Hz), 6.83 d (1H$_{arom.}$, *J* 8.1 Hz), 6.95–6.97 m (2H$_{arom.}$), 7.22 d (2H$_{arom.}$, *J* 8.1 Hz), 7.53 d (2H$_{arom.}$, *J* 8.1 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 21.2 (Me), 56.1 (OMe), 56.1 (OMe), 77.4 q (C^2, *J* 28.8 Hz), 109.4, 111.3, 120.5, 124.7, 125.3 q (CF_3, J_{C-F} 285.8 Hz), 126.9, 128.8, 129.2, 133.5, 134.8, 138.8, 149.3, 149.8. ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: −78.49 c (CF_3). HRMS: $C_{19}H_{19}F_3O_3Ag$ found 459.0328 $[M + Ag]^+$; calcd 459.0332.

(*E*)-1,1,1-Trifluoro-2-(3,4-dimethylphenyl)-2-phenylbut-3-en-2-ol (2j). Yield 93%. Yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 2.28 s (3H, Me), 2.30 s (3H, Me), 2.61 s (1H, OH), 6.70 d (1H, =CH, *J* 16.1 Hz), 6.89 d (1H, =CH, *J* 16.1 Hz), 7.17 d (1H$_{arom.}$, *J* 8.0 Hz), 7.27–7.36 m (4H$_{arom.}$), 7.40 s (1H$_{arom.}$), 7.42–7.44 m (2H$_{arom.}$). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 19.5 (Me), 20.1 (Me), 77.3 q (C^2, J_{C-F} 28.8 Hz), 124.3, 125.3 q (CF_3, J_{C-F} 286.0 Hz), 126.9, 127.0, 127.9, 128.6, 128.8, 129.7, 133.2, 135.1, 135.9, 136.8, 137.4. ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: −78.50 c (CF_3). HRMS: $C_{18}H_{17}F_3OAg$ found 413.0269 $[M + Ag]^+$; calcd 413.0277.

(*E*)-1,1,1-Trifluoro-2-(2,4,6-trimethylphenyl)-2-phenylbut-3-en-2-ol (2m). Yield 94%. Yellow solid. M.p. 66–68 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 2.25 s (3H, Me), 2.28 s (3H, Me), 2.41 s (3H, Me), 2.55 s (1H, OH), 6.67 d (1H, =CH, *J* 16.2 Hz), 6.75 d (1H, =CH, *J* 16.2 Hz), 6.99 s (1H$_{arom.}$), 7.27–7.37 m (3H$_{arom.}$), 7.42–7.43 m (3H$_{arom.}$). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 19.3 (Me), 19.6 (Me), 22.0 q (Me, *J* 1.2 Hz), 78.9 q (C^2, J_{C-F} 28.6 Hz), 125.7 q (CF_3, J_{C-F} 286.7 Hz), 126.9, 127.5, 128.6, 128.9, 129.2, 132.8, 133.7, 134.0, 134.5, 135.1, 135.9, 137.4. ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: −76.72 c (CF_3). HRMS: $C_{19}H_{19}F_3OAg$ found 427.0422 $[M + Ag]^+$; calcd 427.0433.

(*E*)-1,1,1-Trifluoro-4-(3,4-methylenedioxyphenyl)-2-phenylbut-3-en-2-ol (2n). Yield 72%. Yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 2.70 s (1H, OH), 5.97 s (2H, CH_2) 6.54 d (1H, =CH, *J* 16.0 Hz), 6.77 d (1H$_{arom.}$, *J* 8.1 Hz), 6.77 d (1H, =CH, *J* 16.0 Hz), 6.85 dd (1H$_{arom.}$, *J* 8.1 Hz, *J* 1.5 Hz), 6.97 d (1H$_{arom.}$, *J* 1.5 Hz), 7.36–7.43 m (3H$_{arom.}$), 7.63–7.64 m (2H$_{arom.}$). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 77.4 q (C^2, *J* 29.2 Hz), 101.4, 106.1, 108.5, 122.2, 124.8, 125.2 q (CF_3, J_{C-F} 285.8 Hz), 127.0, 128.5, 128.9, 130.1, 133.4, 137.6, 148.2, 148.4. ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: −78.57 c (CF_3). HRMS: $C_{17}H_{13}F_3O_3Ag$ found 428.9867 $[M + Ag]^+$; calcd 428.9863.

(*E*)-1,1,1-Trifluoro-4-(4-chlorophenyl)-2-phenylbut-3-en-2-ol (2o). Yield 93%. Yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 2.69 s (1H, OH), 6.68 d (1H, =CH, *J* 16.0 Hz), 6.85 d (1H, =CH, *J* 16.0 Hz), 7.30–7.45 m (7H$_{arom.}$), 7.63–7.65 m (2H$_{arom.}$). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 77.5 q (C^2, J_{C-F} 29.1 Hz), 125.1 q (CF_3, J_{C-F} 286.0 Hz), 126.8, 127.2, 128.3, 128.6, 129.0, 132.5, 134.2, 134.5, 137.4. ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: −78.40 c (CF_3). HRMS: $C_{16}H_{12}F_3{}^{35}ClOAg$ found 418.9557 $[M + Ag]^+$; calcd 418.9574.

Synthesis and characterization of indenes 3

General procedure for cyclization of compounds 1 or 2 into indenes 3 in H_2SO_4. 1 mL of H_2SO_4 (95%) was added in one portion to a solution of 0.1 mmol of compound **1** or **2** in 1 mL of CH_2Cl_2 at room temperature with vigorous stirring. The reaction mixture was stirred for 2 min, then poured into 15 mL of water, and extracted with CH_2Cl_2 (3 × 15 mL). The combined extracts were washed with water (3 × 10 mL), dried over Na_2SO_4. Evaporation of the solvent under reduced pressure finally gave indene **3**. Analogously the reactions were carried out in CF_3CO_2H (see Table 1).

3-(Trifluoromethyl)-1-phenyl-1*H*-indene (3a). Yield 90%. Yellow solid. M.p. 43–45 °C (oil lit.[13]). ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 4.74 m (1H, C^1H), 7.03 m (1H, =CH), 7.12 d (2H$_{arom.}$, *J* 7.6 Hz), 7.28–7.33 m (5H$_{arom.}$), 7.38 t (1H$_{arom.}$, *J* 7.4 Hz), 7.57 d (1H$_{arom.}$, *J* 7.6 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 55.6 (C^1), 121.2, 122.5 q (CF_3, *J* 270.0 Hz), 123.9, 126.6, 127.0, 127.6, 128.03, 129.1, 134.6 q (C^3, *J* 34.3 Hz), 137.1, 138.2, 141.0 q (C^2, *J* 5.0 Hz), 148.0. ^{19}F {1H} NMR ($CDCl_3$, 376 MHz) δ, ppm: −64.05 s (CF_3). HRMS (MALDI): $C_{16}H_{12}F_3$ found 261.0886 $[M + H]^+$, calcd 261.0891.

3-(Trifluoromethyl)-6-methyl-1-phenyl-1*H*-indene (3b). Yield 99%. Yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 2.36 c (3H, Me), 4.69 m (1H, C^1H), 6.95 m (1H, =CH), 7.12 d (2H$_{arom.}$, *J* 8.0 Hz), 7.13 c (1H$_{arom.}$), 7.19 d (1H$_{arom.}$, *J* 7.8 Hz), 7.28–7.34 m (3H$_{arom.}$), 7.44 d (1H$_{arom.}$, *J* 7.8 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 21.6 (Me), 55.4 (C^1), 120.6, 122.6 q (CF_3, *J* 270.0 Hz), 125.3, 127.5, 128.1, 128.3, 129.1, 134.5 q (C^3, *J* 34.2 Hz), 135.5 d (C^{3a}, *J* 1.1 Hz), 137.0, 137.4 d (C^{7a}, *J* 0.8 Hz), 140.0 q (C^2, *J* 5.1 Hz), 148.4. ^{19}F {1H} NMR ($CDCl_3$, 376 MHz) δ, ppm: −64.07 s (CF_3). HRMS (MALDI): $C_{17}H_{14}F_3$ found 275.1042 $[M + H]^+$, calcd 275.1048.

3-(Trifluoromethyl)-1-(4-methylphenyl)-1*H*-indene (3c). Yield 99%. Yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 2.34 c (3H, Me), 4.71 m (1H, C^1H), 7.00 d (2H$_{arom.}$, *J* 8.1 Hz), 7.01 m (1H, =CH), 7.12 d (2H$_{arom.}$, *J* 8.1 Hz), 7.26–7.32 m (2H$_{arom.}$), 7.37 t.d (1H$_{arom.}$, *J* 7.6 Hz, *J* 1.5 Hz), 7.56 d (1H$_{arom.}$, *J* 7.6 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 21.2 (Me), 55.3 (C^1), 120.9, 122.6 q (CF_3, *J* 270.0 Hz), 124.5, 126.9, 127.4, 127.9, 129.8, 133.9, 134.4 q (C^3, *J* 34.2 Hz), 137.3, 138.2, 141.3 q (C^2, *J* 5.0 Hz), 148.2. ^{19}F {1H} NMR ($CDCl_3$, 376 MHz) δ, ppm: −64.02 s (CF_3). HRMS (MALDI): $C_{17}H_{14}F_3$ found 275.1042 $[M + H]^+$, calcd 275.1038.

3-(Trifluoromethyl)-6-methyl-1-(4-methylphenyl)-1*H*-indene (3d). Yield 99%. Yellow solid. M.p. 101–103 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 2.35 c (3H, Me), 2.36 c (3H, Me), 4.66 m (1H, C^1H), 6.93 m (1H, =CH), 7.00 d (2H$_{arom.}$,

J 7.8 Hz), 7.12 s (1H$_{arom.}$), 7.13 d (2H$_{arom.}$, *J* 7.8 Hz), 7.18 d (1H$_{arom.}$, *J* 7.9 Hz), 7.43 d (1H$_{arom.}$, *J* 7.9 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) *δ*, ppm: 21.2 (Me), 21.6 (Me), 55.1 (C^1), 120.5, 122.6 q (CF_3, *J* 270.0 Hz), 125.3, 127.9, 128.2, 129.8, 134.3, 134.3 q (C^3, *J* 34.2 Hz), 135.5, 137.0, 137.2, 140.2 q (C^2, *J* 5.1 Hz). ^{19}F {1H} NMR ($CDCl_3$, 376 MHz) *δ*, ppm: −64.05 s (CF_3). HRMS (MALDI): $C_{18}H_{16}F_3$ found 289.1199 $[M + H]^+$, calcd 289.1210.

3-(Trifluoromethyl)-6-methoxy-1-phenyl-1*H*-indene (3e). Yield 97%. Yellow solid. M.p. 77–79 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) *δ*, ppm: 3.79 c (3H, OMe), 4.69 m (1H, C^{1}H), 6.84 d (2H$_{arom.}$, *J* 8.6 Hz), 6.99 m (1H, =CH), 7.01 d (2H$_{arom.}$, *J* 8.6 Hz), 7.25–7.30 m (2H$_{arom.}$), 7.37 m (1H$_{arom.}$), 7.54 d (1H$_{arom.}$, *J* 7.5 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) *δ*, ppm: 54.9 (C^1), 55.4 (OMe), 114.5, 120.9, 122.6 q (CF_3, *J* 270.0 Hz), 124.5, 126.9, 127.4, 128.8, 129.0, 134.3 q (C^3, *J* 34.2 Hz), 138.1, 141.4 q (C^2, *J* 5.0 Hz), 148.3, 159.1. ^{19}F {1H} NMR ($CDCl_3$, 376 MHz) *δ*, ppm: −64.03 s (CF_3). HRMS (MALDI): $C_{17}H_{14}F_3O$ found 291.0991 $[M + H]^+$, calcd 291.0998.

3-(Trifluoromethyl)-1-(4-methoxyphenyl)-1*H*-indene (3f). Yield 97%. Yellow solid. M.p. 81–82 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) *δ*, ppm: 3.79 c (3H, OMe), 4.69 m (1H, C^{1}H), 6.84 d (2H$_{arom.}$, *J* 8.7 Hz), 7.00 m (1H, =CH), 7.02 d (2H$_{arom.}$, *J* 8.7 Hz), 7.25–7.31 m (2H$_{arom.}$), 7.36 m (1H$_{arom.}$), 7.55 d (1H$_{arom.}$, *J* 7.6 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) *δ*, ppm: 54.9 (C^1), 55.4 (OMe), 114.5, 120.9, 122.6 q (CF_3, *J* 270.0 Hz), 124.5, 126.9, 127.4, 128.8, 129.0, 134.3 q (C^3, *J* 34.2 Hz), 138.1, 141.4 q (C^2, *J* 5.0 Hz), 148.3, 159.1. ^{19}F {1H} NMR ($CDCl_3$, 376 MHz) *δ*, ppm: −64.02 s (CF_3). HRMS (MALDI): $C_{17}H_{14}F_3O$ found 291.0991 $[M + H]^+$, calcd 291.1002.

3-(Trifluoromethyl)-5,6-dimethoxy-1-phenyl-1*H*-indene (3g). Yield 95%. Yellow solid. M.p. 60–62 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) *δ*, ppm: 3.81 c (3H, OMe), 3.95 c (3H, OMe), 4.65 m (1H, C^{1}H), 6.84 c (1H$_{arom.}$), 6.90 m (1H, =CH), 7.05 c (1H$_{arom.}$), 7.08–7.10 m (2H$_{arom.}$), 7.27–7.33 m (3H$_{arom.}$). ^{13}C NMR ($CDCl_3$, 100 MHz) *δ*, ppm: 55.6 (C^1), 56.3 (OMe), 56.4 (OMe), 104.0, 108.1, 122.6 q (CF_3, *J* 269.9 Hz), 127.5, 128.0, 129.1, 130.8, 134.0 q (C^3, *J* 34.1 Hz), 137.4, 139.8 q (C^2, *J* 5.2 Hz), 140.9, 149.0. ^{19}F {1H} NMR ($CDCl_3$, 376 MHz) *δ*, ppm: −63.95 s (CF_3). HRMS (MALDI): $C_{18}H_{16}F_3O_2$ found 321.1097 $[M + H]^+$, calcd 321.1095.

3-(Trifluoromethyl)-6-methoxy-1-(4-methoxyphenyl)-1*H*-indene (3h). Yield 92%. Yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) *δ*, ppm: 3.77 c (3H, OMe), 3.79 c (3H, OMe), 4.63 m (1H, C^{1}H), 6.84 d (2H$_{arom.}$, *J* 8.6 Hz), 6.85 m (=CH + 1H$_{arom.}$), 6.89 dd (1H$_{arom.}$, *J* 8.3 Hz, *J* 2.3 Hz), 7.01 d (2H$_{arom.}$, *J* 8.6 Hz), 7.42 d (H$_{arom.}$, *J* 8.4 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) *δ*, ppm: 54.8 (C^1), 55.4 (OMe), 55.7 (OMe), 110.9, 113.0, 114.5, 121.4, 122.6 q (CF_3, *J* 269.9 Hz), 129.0, 129.2, 131.0, 133.8 q (C^3, *J* 34.1 Hz), 139.2 q (C^2, *J* 5.1 Hz), 150.4, 159.1, 159.5. ^{19}F {1H} NMR ($CDCl_3$, 376 MHz) *δ*, ppm: −64.11 s (CF_3). HRMS (MALDI): $C_{18}H_{16}F_3O_2$ found 321.1097 $[M + H]^+$, calcd 321.1115.

3-(Trifluoromethyl)-6-methyl-1-(3,4-dimethoxyphenyl)-1*H*-indene (3i). Yield 50%. Yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) *δ*, ppm: 2.44 c (3H, Me), 3.88 c (6H, 2OMe), 4.67 m (1H, C^{1}H), 6.92 m (1H, =CH), 7.2–7.5 m (6H$_{arom.}$). ^{13}C NMR ($CDCl_3$, 100 MHz) *δ*, ppm: 21.4 (Me), 42.2 (C^1), 56.1 (2OMe), 111.3, 120.4, 123.5 q (CF_3, *J* 273.3Hz), 125.3, 127.6, 129.8, 130.2, 139.2, 139.4 q (C^3, *J* 34 Hz), 140.1 q (C^2, *J* 5.0Hz), 148.6. ^{19}F {^{1}H} NMR ($CDCl_3$, 376 MHz) *δ*, ppm: −64.04 s (CF_3). HRMS (MALDI): $C_{19}H_{18}F_3O_2$ found 335.1253 $[M + H]^+$, calcd 335.1267.

3-(Trifluoromethyl)-5,6-dimethyl-1-phenyl-1*H*-indene (3j1), and 3-(trifluoromethyl)-6,7-dimethyl-1-phenyl-1*H*-indene (3j2). Yield 96%. Colorless solid. M.p. 85–88 °C (for ratio of **3j1 : 3j2** 1.25 : 1). Compound **3j1**: ^{1}H NMR ($CDCl_3$, 400 MHz) (from the spectrum of a mixture of isomers) *δ*, ppm: 2.26 s (3H, Me), 2.34 s (3H, Me), 4.67 m (1H, C^{1}H), 6.93 m (1H, =CH), 7.08 c (1H$_{arom.}$), 7.10–7.12 m (2H$_{arom.}$, *J* 1.5 Hz), 7.22 d (1H$_{arom.}$, *J* 7.7 Hz), 7.24–7.31 m (3H$_{arom.}$). ^{13}C NMR ($CDCl_3$, 100 MHz) (from the spectrum of a mixture of isomers, some signals) *δ*, ppm: 20.1 (Me), 20.2 (Me), 55.2 (C^1), 122.64 q (CF_3, *J* 270.0 Hz), 134.5 q (C^3, *J* 34.1 Hz), 140.1 q (C^2, *J* 5.1 Hz). ^{19}F {^{1}H} NMR ($CDCl_3$, 376 MHz) (from the spectrum of a mixture of isomers) *δ*, ppm: −64.00 s (CF_3) Mass spectrum (GC-MS), *m*/*z* (I$_{otH.}$, %): 288 $[M]^+$ (100). Compound **3j2**: ^{1}H NMR ($CDCl_3$, 400 MHz) (from the spectrum of a mixture of isomers) *δ*, ppm: 1.99 c (3H, Me), 2.30 c (3H, Me), 4.72 m (1H, C^{1}H), 6.86 m (1H, =CH), 7.03–7.05 m (2H$_{arom.}$), 7.24–7.31 m (4H$_{arom.}$), 7.34 c (1H$_{arom.}$). ^{13}C NMR ($CDCl_3$, 100 MHz) (from the spectrum of a mixture of isomers) *δ*, ppm: 15.8 (Me), 19.8 (Me), 55.4 (C^1), 122.62 q (CF_3, *J* 270.0 Hz), 133.4 q (C^3, *J* 34.1 Hz), 140.9 q (C^2, *J* 5.1 Hz). ^{19}F {^{1}H} NMR ($CDCl_3$, 376 MHz) (from the spectrum of a mixture of isomers) *δ*, ppm: −64.10 s (CF_3). For a mixture of isomers: 7.24–7.31 m (3H$_{arom.}^{A}$ + 4H$_{arom.}^{B}$). Mass spectrum (GC-MS), *m*/*z* (I$_{otH.}$, %): 288 $[M]^+$ (80). ^{13}C NMR ($CDCl_3$, 100 MHz) *δ*, ppm: 118.1, 121.9, 125.7, 127.3, 127.5, 128.0, 129.1, 129.5, 133.4, 135.6, 135.8, 135.9, 136.1, 136.7, 136.8, 137.7, 145.9, 146.1. HRMS (MALDI): $C_{18}H_{16}F_3$ found 289.1199 $[M + H]^+$, calcd 289.1204 (for a mixture of isomers).

3-(Trifluoromethyl)-4,6-dimethyl-1-phenyl-1*H*-indene (3k). Yield 97%. Yellow solid. M.p. 111–113 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) *δ*, ppm: 2.35 c (3H, Me), 2.59 c (3H, Me), 4.64 m (1H, C^{1}H), 7.00 c (1H$_{arom.}$), 7.03 c (1H$_{arom.}$), 7.09 m (1H, =CH), 7.15 d (2H$_{arom.}$, *J* 6.6 Hz), 7.30–7.37 m (3H$_{arom.}$). ^{13}C NMR ($CDCl_3$, 100 MHz) *δ*, ppm: 20.0 q (Me, *J* 4.7 Hz), 21.2 (Me), 54.6 (C^1), 122.9 q (CF_3, *J* 269.4 Hz), 123.1, 127.5, 128.1, 129.1, 131.3, 131.4, 133.8, 134.5 q (C^3, *J* 33.9 Hz), 137.0, 137.8, 141.8 q (C^2, *J* 6.3 Hz), 149.8. ^{19}F {^{1}H} NMR ($CDCl_3$, 376 MHz) *δ*, ppm: −60.61 s (CF_3). HRMS (MALDI): $C_{18}H_{16}F_3$ found 289.1199 $[M + H]^+$, calcd 289.1214.

3-(Trifluoromethyl)-4,7-dimethyl-1-phenyl-1*H*-indene (3l). Yield 97%. Yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) *δ*, ppm: 2.01 c (3H, Me), 2.55 c (3H, Me), 4.64 m (1H, C^{1}H), 6.98 d (1H$_{arom.}$, *J* 7.7 Hz), 7.02–7.05 m (=CH + 2H$_{arom.}$), 7.12 d (1H$_{arom.}$, *J* 7.7 Hz), 7.23–7.30 m (3H$_{arom.}$). ^{13}C NMR ($CDCl_3$, 100 MHz) *δ*, ppm: 18.7 (Me), 19.8 q (Me, *J* 4.8 Hz), 54.5 (C^1), 122.9 q (CF_3, *J* 269.4 Hz), 127.3, 128.1, 128.6, 129.0, 129.2, 131.1, 131.9, 133.5 q (C^3, *J* 33.9 Hz), 136.3, 137.0, 143.7 q (C^2, *J* 6.4 Hz), 146.9. ^{19}F {^{1}H} NMR ($CDCl_3$, 376 MHz) *δ*, ppm: −60.50 s (CF_3). HRMS (MALDI): $C_{18}H_{16}F_3$ found 289.1199 $[M + H]^+$, calcd 289.1208.

3-(Trifluoromethyl)-4,6,7-trimethyl-1-phenyl-1*H*-indene (3m). Yield 97%. Yellow solid. M.p. 59–61 °C. ^{1}H NMR ($CDCl_3$,

400 MHz) δ, ppm: 1.94 c (3H, Me), 2.26 c (3H, Me), 2.51 c (3H, Me), 4.65 m (1H, C^1H), 6.96 c (1$H_{arom.}$), 7.02–7.03 m (=CH + 2$H_{arom.}$), 7.21–7.29 m (3$H_{arom.}$). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 15.5 (Me), 19.5 (Me), 19.7 q (Me, J 4.8 Hz), 54.6 (C^1), 122.9 q (CF_3, J 269.4 Hz), 126.9, 127.2, 128.0, 128.6, 129.0, 132.7, 133.2 q (C^3, J 33.8 Hz), 134.9, 135.7, 137.1, 142.8 q (C^2, J 6.4 Hz), 147.2. ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: −60.69 d (CF_3, J 1.8 Hz). HRMS (MALDI): $C_{19}H_{18}F_3$ found 303.1355 $[M + H]^+$, calcd 303.1361.

3-(Trifluoromethyl)-1-(3,4-methylenedioxyphenyl)-1*H*-indene (3n). Yield 91%. Yellow oil. ^1H NMR ($CDCl_3$, 400 MHz) δ, ppm: 4.65 m (1H, C^1H), 5.92 m (2H, AB system, CH_2), 6.45 d (1$H_{arom.}$, J 1.7 Hz), 6.67 dd (1$H_{arom.}$, J 7.9 Hz, J 1.7 Hz), 6.76 d (1$H_{arom.}$, J 7.9 Hz), 6.97 m (1H, =CH), 7.27–7.31 m (2$H_{arom.}$), 7.36 dt (1$H_{arom.}$, J 7.2 Hz, J 1.8 Hz), 7.53 dd (1$H_{arom.}$, J 7.5 Hz, J 0.8 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 55.2 (C^1), 101.3, 108.0, 108.7, 121.0, 121.4, 122.5 q (CF_3, J 270.0 Hz), 124.5, 127.0, 127.5, 134.5 q (C^3, J 34.2 Hz), 138.1, 141.1 q (C^2, J 5.0 Hz), 147.1, 148.1, 148.2. ^{19}F {1H} NMR ($CDCl_3$, 376 MHz) δ, ppm: −64.07 s (CF_3). HRMS (MALDI): $C_{17}H_{12}F_3O_2$ found 305.0784 $[M + H]^+$, calcd 305.0792.

1-(4-Chlorophenyl)-3-(trifluoromethyl)-1*H*-indene (3o). Yield 97%. Yellow solid. M.p. 53–55 °C. ^1H NMR ($CDCl_3$, 400 MHz) δ, ppm: 4.71 m (1H, C^1H), 7.00 m (1H, =CH), 7.05 d (2$H_{arom.}$, J 7.7 Hz), 7.28–7.30 m (4$H_{arom.}$), 7.37–7.43 m (1$H_{arom.}$), 7.59 d (1$H_{arom.}$, J 6.9 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 54.9 (C^1), 121.1, 122.4 q (CF_3, J 270.0 Hz), 124.5, 127.2, 127.7, 129.3, 129.4, 133.5, 135.0 q (C^3, J 34.4 Hz), 135.6, 138.1, 140.5 q (C^2, J 4.9 Hz), 147.6. ^{19}F {1H} NMR ($CDCl_3$, 376 MHz) δ, ppm: −64.04 s (CF_3). HRMS (MALDI): $C_{16}H_{11}F_3{}^{35}Cl$ found 295.0496 $[M + H]^+$, calcd 295.0503.

6-Fluoro-3-(trifluoromethyl)-1-(3,4-dimethylphenyl)-1*H*-indene (3p). Yield 97%. Yellow oil. ^1H NMR ($CDCl_3$, 400 MHz) δ, ppm: 2.23 s (3H, Me), 2.25 s (3H, Me), 4.65 m (1H, C^1H), 6.83–6.85 m (2$H_{arom.}$), 6.97–6.98 m (1$H_{arom.}$, C^2H), 7.02 dd (1$H_{arom.}$, $^3J_{H-F}$ 8.8 Hz, ^4J 2.3 Hz), 7.04–7.10 m (2$H_{arom.}$), 7.47 dd (1$H_{arom.}$, J 7.8 Hz, $^4J_{H-F}$ 5.0 Hz).^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 19.5 (Me), 19.9 (Me), 55.3 d (C^1, J_{C-F} 2.3 Hz), 112.4 d (J_{C-F} 23.5 Hz), 114.5 d (J_{C-F} 23.5 Hz), 121.8 d (J_{C-F} 8.3 Hz), 122.4 q (CF_3, J_{C-F} 269.9 Hz), 125.4, 129.0, 130.4, 133.4, 133.7 q (C^3, J_{C-F} 34.5 Hz), 134.1 q (J_{C-F} 1.1 Hz), 136.3, 137.6, 141.1 quintet (C^4, J_{C-F} 4.9 Hz), 150.9 d (J_{C-F} 8.3 Hz), 162.6 d (C^6, J_{C-F} 246.4 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: −114.91 td (F, $^3J_{H-F}$ 8.8 Hz, $^4J_{H-F}$ 5.0 Hz), −64.14 s (CF_3). HRMS (MALDI): $C_{18}H_{15}F_4$ found 307.1104 $[M + H]^+$, calcd 307.1089.

6-Fluoro-3-(trifluoromethyl)-1-(3,4-dimethoxyphenyl)-1*H*-indene (3q). Yield 74%. Yellow oil. ^1H NMR ($CDCl_3$, 400 MHz) δ, ppm: 3.81 s (3H, OMe), 3.86 s (3H, OMe), 4.64 m (1H, C^1H), 6.51 d (1$H_{arom.}$, ^4J 2.0 Hz), 6.69 dd (1$H_{arom.}$, ^3J 8.2 Hz, ^4J 2.0 Hz), 6.81 d (1H, C^2H, ^3J 8.2 Hz), 6.97–6.99 m (1$H_{arom.}$, C^2H), 7.01 dd (1$H_{arom.}$, $^3J_{H-F}$ 8.8 Hz, ^4J 2.2 Hz), 7.06 td (1$H_{arom.}$, $^3J_{H-F}$ 8.8 Hz, ^4J 2.2 Hz), 7.47 dd (1$H_{arom.}$, ^3J 7.7 Hz, $^4J_{H-F}$ 4.9 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 55.3 d (C^1, J_{C-F} 2.4 Hz), 56.1 (2MeO), 110.9, 111.8, 112.3 d (J_{C-F} 23.5 Hz), 114.7 d (J_{C-F} 23.5 Hz), 120.3, 121.9 d (J_{C-F} 8.8 Hz), 122.4 q (CF_3, J_{C-F} 269.9 Hz), 128.6.4, 133.7 q (C^3, J_{C-F} 34.6 Hz), 133.9, 140.9 quintet (C^4, J_{C-F} 4.9 Hz), 148.9, 149.6, 150.5 d (J_{C-F} 8.3 Hz), 162.6 d (C^6, J_{C-F} 246.6 Hz).^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: −114.72 td (F, $^3J_{H-F}$ 8.8 Hz, $^4J_{H-F}$ 4.9 Hz), −64.15 s (CF_3). HRMS (MALDI): $C_{18}H_{15}F_4O_2$ found 339.1003 $[M + H]^+$, calcd 339.1018.

Synthesis and characterization of indenes 4

General procedure for isomerization of indenes 3 into 4. A suspension of 4 g of silica gel in a solution of 0.1 mmol of indene **3** in 5 mL of EtOAc was stirred at room temperature for 4 h. The silica gel was filtered off, and washed with EtOAc (3 × 20 mL). The solutions in EtOAc were combined, and evaporation of the solvent under reduced pressure quantitatively gave indene **4**.

1-(Trifluoromethyl)-3-phenyl-1*H*-indene (4a). Quantitative yield. Yellow solid. M.p. 50–52 °C (lit.[13] m.p. 49–51 °C). ^1H NMR ($CDCl_3$, 400 MHz) δ, ppm: 4.24 qd (1H, C^1H, J 9.4 Hz, J 2.0 Hz), 6.41 d (1H, =CH, J 2.0 Hz), 7.32 t (1$H_{arom.}$, J 7.5 Hz), 7.40–7.50 m (4$H_{arom.}$), 7.55–7.62 m (3$H_{arom.}$), 7.65 d (1$H_{arom.}$, J 7.5 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 52.7 q (C^1, J 29.4 Hz), 121.3, 124.8 q (C^2, J 2.7 Hz), 124.9, 126.3 q (CF_3, J 278.5 Hz), 126.4, 127.8, 128.5, 128.8, 129.5, 134.6, 138.8, 144.2, 149.4. ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: −67.35 dd (CF_3, J 9.3 Hz, J 0.7 Hz). HRMS (MALDI): $C_{16}H_{12}F_3$ found 261.0886 $[M + H]^+$, calcd 261.0885.

1-(Trifluoromethyl)-3-(4-methylphenyl)-1*H*-indene (4c). Quantitative yield. Yellow oil. ^1H NMR ($CDCl_3$, 400 MHz) δ, ppm: 2.44 c (3H, Me), 4.24 qd (1H, C^1H, J 9.3 Hz, J 2.0 Hz), 6.40 d (1H, =CH, J 2.0 Hz), 7.30 d (2$H_{arom.}$, J 7.9 Hz), 7.34 t (1$H_{arom.}$, J 7.5 Hz), 7.43 t (1$H_{arom.}$, J 7.5 Hz), 7.52 d (2$H_{arom.}$, J 7.9 Hz), 7.58 d (1$H_{arom.}$, J 7.5 Hz), 7.68 d (1$H_{arom.}$, J 7.5 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 21.6 (Me), 52.7 q (C^1, J 29.5 Hz), 121.3, 124.2 q (C^2, J 2.7 Hz), 124.9, 126.3 q (CF_3, J 278.5 Hz), 126.4, 127.7, 128.5, 129.5, 131.8, 138.5, 138.9 q (J 1.6 Hz), 144.4, 149.3. ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: −67.31 d (CF_3, J 9.3 Hz). HRMS (MALDI): $C_{17}H_{14}F_3$ found 275.1042 $[M + H]^+$, calcd 275.1047.

1-(Trifluoromethyl)-5-methyl-3-(4-methylphenyl)-1*H*-indene (4d). Quantitative yield. Yellow oil. ^1H NMR ($CDCl_3$, 400 MHz) δ, ppm: 2.43 c (3H, Me), 2.44 c (3H, Me), 4.21 br. q (1H, C^1H, J 9.2 Hz), 6.38 d (1H, =CH, J 2.1 Hz), 7.16 d (1$H_{arom.}$, J 7.6 Hz), 7.30 d (2$H_{arom.}$, J 7.9 Hz), 7.38 s (2$H_{arom.}$), 7.51 d (2$H_{arom.}$, J 7.9 Hz), 7.55 d (1$H_{arom.}$, J 7.6 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 21.4 (Me), 21.8 (Me), 52.4 (C^1, J 29.4 Hz), 122.1, 124.5 q (C^2, J 2.8 Hz), 124.6, 126.4 q (CF_3, J 278.4 Hz), 127.1, 127.8, 129.5, 131.9, 136.0 q (J 1.8 Hz), 138.4, 138.5, 144.6, 149.3. ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: −67.49 d (CF_3, J 9.4 Hz). HRMS (MALDI): $C_{18}H_{16}F_3$ found 289.1199 $[M + H]^+$, calcd 289.1209.

1-(Trifluoromethyl)-5-methoxy-3-phenyl-1*H*-indene (4e). Quantitative yield. Yellow solid. M.p. 77–79 °C. ^1H NMR ($CDCl_3$, 400 MHz) δ, ppm: 3.87 c (3H, OMe), 4.23 qd (1H, C^1H, J 9.3 Hz, J 2.1 Hz), 6.35 d (1H, =CH, J 2.1 Hz), 7.01 d (2$H_{arom.}$, J 8.8 Hz), 7.33 dt (1$H_{arom.}$, J 7.4 Hz, J 0.9 Hz), 7.42 t (1$H_{arom.}$, J 7.4 Hz), 7.54–7.58 m (3$H_{arom.}$), 7.66 d (1$H_{arom.}$, J 7.4 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 52.7 q (C^1, J 29.4 Hz), 55.5

(OMe), 114.3, 121.3, 123.7 q (C^2, *J* 2.8 Hz), 124.9, 126.3 q (CF_3, *J* 278.5 Hz), 127.2, 128.5, 129.1, 138.9, 144.5, 148.9, 160.0. ^{19}F NMR ($CDCl_3$, 376 MHz) *δ*, ppm: −67.34 d (CF_3, *J* 9.5 Hz). HRMS (MALDI): $C_{17}H_{14}F_3O$ found 291.0991 $[M + H]^+$, calcd 291.0990.

1-(Trifluoromethyl)-5,6-dimethoxy-3-phenyl-1*H*-indene (4g). Quantitative yield. Yellow solid. M.p. 86–88 °C. ^1H NMR ($CDCl_3$, 400 MHz) *δ*, ppm: 3.89 c (3H, OMe), 3.95 c (3H, OMe), 4.18 br. q (1H, C^1H, *J* 9.3 Hz), 6.32 d (1H, =CH, *J* 1.9), 7.07 c ($1H_{arom.}$), 7.22 c ($1H_{arom.}$), 7.43 t ($1H_{arom.}$, *J* 7.3 Hz), 7.49 t ($2H_{arom.}$, *J* 7.3 Hz), 7.59 d ($2H_{arom.}$, *J* 7.3 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) *δ*, ppm: 52.5 q (C^1, *J* 29.4 Hz), 56.3 (OMe), 56.5 (OMe), 104.9, 108.8, 123.5 q (C^2, *J* 2.8 Hz), 126.3 q (CF_3, *J* 278.5 Hz), 127.7, 128.6, 128.9, 131.3, 135.0, 137.3, 148.4, 149.2, 149.8. ^{19}F NMR ($CDCl_3$, 376 MHz) *δ*, ppm: −67.58 d (CF_3, *J* 9.3 Hz). HRMS (MALDI): $C_{18}H_{16}F_3O_2$ found 321.1097 $[M + H]^+$, calcd 321.1097.

1-(Trifluoromethyl)-5-methyl-3-(3,4-dimethoxyphenyl)-1*H*-indene (4i). Quantitative yield. Yellow oil. ^1H NMR ($CDCl_3$, 400 MHz) *δ*, ppm: 2.42 (3H, Me), 3.95 (3H, OMe), 3.95 (3H, OMe), 4.20 qd (1H, C^1H, *J* 9.3 Hz, *J* 1.9 Hz), 6.35 d (1H, =CH, *J* 1.9 Hz), 6.98 d ($1H_{arom.}$, *J* 8.2 Hz), 7.09 d ($1H_{arom.}$, *J* 1.9 Hz), 7.14–7.19 m ($2H_{arom.}$), 7.38 c ($1H_{arom.}$), 7.54 d ($1H_{arom.}$, *J* 7.6 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) *δ*, ppm: 21.8 (Me), 52.3 q (C^1, *J* 29.5 Hz), 56.1 (OMe), 56.2 (OMe), 111.2, 111.4, 120.4, 122.0, 124.2 q (C^2, *J* 2.7 Hz), 124.6, 126.3 q (CF_3, *J* 278.4 Hz), 127.2, 127.6, 136.0 d (*J* 1.9 Hz), 138.5, 144.6, 149.1, 149.3 149.5. ^{19}F NMR ($CDCl_3$, 376 MHz) *δ*, ppm: −67.48 d (CF_3, *J* 9.3 Hz). HRMS (MALDI): $C_{19}H_{18}F_3O_2$ found 335.1253 $[M + H]^+$, calcd 335.1258.

1-(Trifluoromethyl)-5,6-dimethyl-3-phenyl-1*H*-indene (4j1). **4j1** was obtained as a mixture with **3j2**. Quantitative yield. A yellow oily mixture of isomers. Compound **4j1**: ^1H NMR ($CDCl_3$, 400 MHz) (from the spectrum of a mixture of isomers) *δ*, ppm: 2.32 c (3H, Me), 2.35 c (3H, Me), 4.19 qd (1H, C^1H, *J* 9.0 Hz, *J* 2.0 Hz), 6.33 d (1H, =CH, *J* 2.0 Hz), 7.27–7.31 m ($1H_{arom.}$), 7.40–7.50 m ($4H_{arom.}$), 7.60 d ($2H_{arom.}$, *J* 8.4 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) (from the spectrum of a mixture of isomers, some signals) *δ*, ppm: 20.1 (Me), 20.3 (Me), 55.4 q (C^1, *J* 29.4 Hz), 124.0 q (C^2, *J* 2.6 Hz), 126.4 q (CF_3, *J* 278.5 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz) (from the spectrum of a mixture of isomers) *δ*, ppm: −67.45 d (CF_3, *J* 9.0 Hz). Mass spectrum (GC-MS), *m*/*z* ($I_{otH.}$, %): 288 $[M]^+$ (100). HRMS (MALDI): $C_{18}H_{16}F_3$ found 289.1199 $[M + H]^+$, calcd 289.1202 (for a mixture of isomers).

1-(Trifluoromethyl)-5,7-dimethyl-3-phenyl-1*H*-indene (4k). Quantitative yield. Yellow oil. ^1H NMR ($CDCl_3$, 400 MHz) *δ*, ppm: 2.37 c (3H, Me), 2.46 c (3H, Me), 4.25 qd (1H, C^1H, *J* 8.1 Hz, *J* 2.1 Hz), 6.39 d (1H, =CH, *J* 2.1 Hz), 6.98 c ($1H_{arom.}$), 7.18 c ($1H_{arom.}$), 7.41–7.50 m ($3H_{arom.}$), 7.57–7.59 m ($2H_{arom.}$). ^{13}C NMR ($CDCl_3$, 100 MHz) *δ*, ppm: 20.0 q (Me, *J* 3.7 Hz), 21.5 (Me), 52.0 q (C^1, *J* 29.2 Hz), 119.9, 125.9 q (C^2, *J* 3.1 Hz), 126.7 q (CF_3, *J* 279.9 Hz), 128.0, 128.5, 128.8, 129.7, 134.2, 135.0, 135.2, 138.7, 145.3, 149.4. ^{19}F NMR ($CDCl_3$, 376 MHz) *δ*, ppm: −63.90 dd (CF_3, *J* 8.2 Hz, *J* 1.3 Hz). HRMS (MALDI): $C_{18}H_{16}F_3$ found 289.1199 $[M + H]^+$, calcd 289.1207.

3-(4-Chlorophenyl)-1-(trifluoromethyl)-1*H*-indene (4o). Quantitative yield. Yellow solid. M.p. 49–51 °C. ^1H NMR ($CDCl_3$, 400 MHz) *δ*, ppm: 4.25 qd (1H, C^1H, *J* 9.3 Hz, *J* 2.1 Hz), 6.43 d (1H, =CH, *J* 2.1 Hz), 7.35 dt ($1H_{arom.}$, *J* 7.4 Hz, *J* 0.9 Hz), 7.41–7.46 m ($3H_{arom.}$), 7.50–7.55 m ($3H_{arom.}$), 7.67 d ($1H_{arom.}$, *J* 7.4 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) *δ*, ppm: 52.8 q (C^1, *J* 29.6 Hz), 121.1, 125.1, 125.2 q (C^2, *J* 2.8 Hz), 126.1 q (CF_3, *J* 278.6 Hz), 126.7, 128.7, 129.1, 129.2, 133.1, 134.6, 138.7, 143.9, 148.4. ^{19}F NMR ($CDCl_3$, 376 MHz) *δ*, ppm: −67.23 d (CF_3, *J* 9.3 Hz). HRMS (MALDI): $C_{16}H_{11}F_3Cl$ found 295.0496 $[M + H]^+$, calcd 295.0496.

5-Fluoro-1-(trifluoromethyl)-3-(3,4-dimethylphenyl)-1*H*-indene (4p). Quantitative yield. Yellow oil. ^1H NMR ($CDCl_3$, 400 MHz) *δ*, ppm: 2.36 (3H, Me), 2.37 (3H, Me), 4.22 br. q (1H, C^1H, *J* 9.1 Hz), 6.47 c (1H, =CH), 7.03 dt ($1H_{arom.}$, *J* 8.5 Hz, *J* 2.2 Hz), 7.25–7.35 m ($3H_{arom.}$), 7.37 c ($1H_{arom.}$), 7.60 dd ($1H_{arom.}$, *J* 7.7 Hz, *J* 5.4 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) *δ*, ppm: 19.7 (Me), 20.0 (Me), 52.2 q (C^1, *J* 29.7 Hz), 109.0 d (*J* 24.2 Hz), 113.0 d (*J* 23.2 Hz), 125.1, 125.8 d (*J* 9.3 Hz), 126.0 q (C^2, *J* 2.6 Hz), 126.1 q (CF_3, *J* 278.5 Hz), 128.9, 130.2, 131.6, 134.2 m, 137.4 d (*J* 25.7 Hz), 146.8 d (*J* 9.0 Hz), 148.8 d (*J* 2.9 Hz), 163.6 d (*J* 245.3 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz) *δ*, ppm: −113.55 to −113.48 m ($1F_{arom.}$), −67.52 d (CF_3, *J* 9.1 Hz). HRMS (MALDI): $C_{18}H_{15}F_4$ found 307.1104 $[M + H]^+$, calcd 307.1107.

5-Fluoro-1-(trifluoromethyl)-3-(3,4-dimethoxyphenyl)-1*H*-indene (4q). Quantitative yield. Yellow oil. ^1H NMR ($CDCl_3$, 400 MHz) *δ*, ppm: 3.94 (6H, 2OMe), 4.21 br. q (1H, C^1H, *J* 8.9 Hz), 6.44 d (1H, =CH, *J* 2.1 Hz), 6.97 d ($1H_{arom.}$, *J* 8.2 Hz), 7.02 dt ($1H_{arom.}$, *J* 8.7 Hz, *J* 2.4 Hz), 7.06 d ($1H_{arom.}$, *J* 1.9 Hz), 7.14 dd ($1H_{arom.}$, *J* 8.2 Hz, *J* 1.9 Hz), 7.26 dd ($1H_{arom.}$, *J* 9.0 Hz, *J* 2.4 Hz), 7.58 dd ($H_{arom.}$, *J* 8.0 Hz, *J* 5.1 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) *δ*, ppm: 52.2 q (C^1, *J* 29.8 Hz), 56.1 (OMe), 56.2 (OMe), 108.9 d (*J* 24.3 Hz), 110.9, 111.5, 113.1 d (*J* 23.2 Hz), 120.3, 125.8 q (C^2, *J* 2.6 Hz), 125.9 d (*J* 9.2 Hz), 126.0 q (CF_3, *J* 278.5 Hz), 126.8, 134.1 m, 146.7 d (*J* 8.8 Hz), 148.5 d (*J* 2.9 Hz), 149.6 d (*J* 44.1 Hz), 163.6 d (*J* 245.5 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz) *δ*, ppm: −113.31 dt ($1F_{arom.}$, *J* 9.0 Hz, *J* 5.1 Hz), −67.51 d (CF_3, *J* 8.9 Hz). HRMS (MALDI): $C_{18}H_{15}F_4O_2$ found 339.1003 $[M + H]^+$, calcd 339.1009.

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