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Article

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Friedel-Crafts Alkylation of Arenes with 2-Halogeno-2-CF_3-Styrenes under Superacidic Conditions. Access to Trifluoromethylated Ethanes and Ethenes

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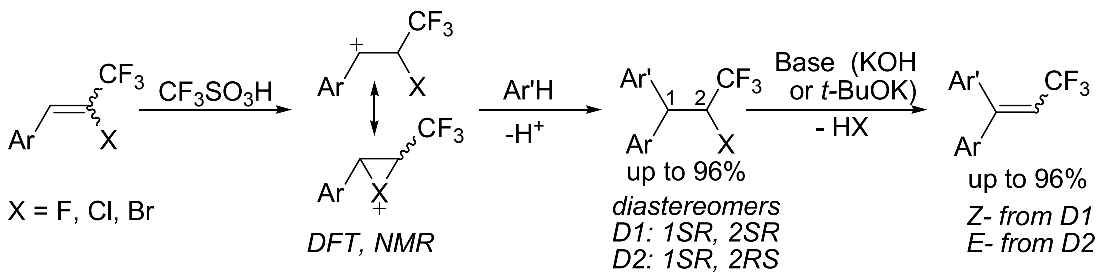
Keywords: trifluoromethyl group, alkenes, superacid, carbocation, hydroarylation, dehydrohalogenation

Graphical abstract



Abstract

The formation of the corresponding benzyl cations [$ArHC^{+}$–$CH(X)CF_3$] takes palace under protonation of *E-/Z*-2-halogeno-2-CF_3 styrenes [$ArCH{=}C(X)CF_3$, X = F, Cl, Br] in superacids. The structure of these new electrophiles were studied by means of NMR and theoretical DFT calculations. Accordingly to these data, in the case of bromo derivatives the formed cations, most probably, exist as cyclic bromonium ions, however in the cases of chloro and fluoro derivatives open forms are more preferable. Subsequent reaction of these benzyl cations with arenes proceeds as Friedel-Crafts alkylation to afford 1,1-diaryl-2-halo-3,3,3-trifluoropropanes [Ar(Ar')CH–$CH(X)CF_3$] in high yields (up to 96%) as a mixture of two diastereomers. The prepared halogenopropanes were easily converted into the corresponding mixtures of *E-/Z*-trifluoromethylated diarylethenes [Ar(Ar')C=CCF_3] (in yields up to 96 %) by dehydrohalogenation with base (KOH or *t*-BuOK). The mechanism of elimination (E_2 and Ecb) depends on nature of leaving group and reaction conditions.

INTRODUCTION

Organofluorine compounds are widely used in chemistry, biology, medicine, nanotechnology, and material science. Trifluoromethyl substituted alkenes are intensively explored as drugs, agrochemicals, liquid crystals, etc. (Figure 1).[1]

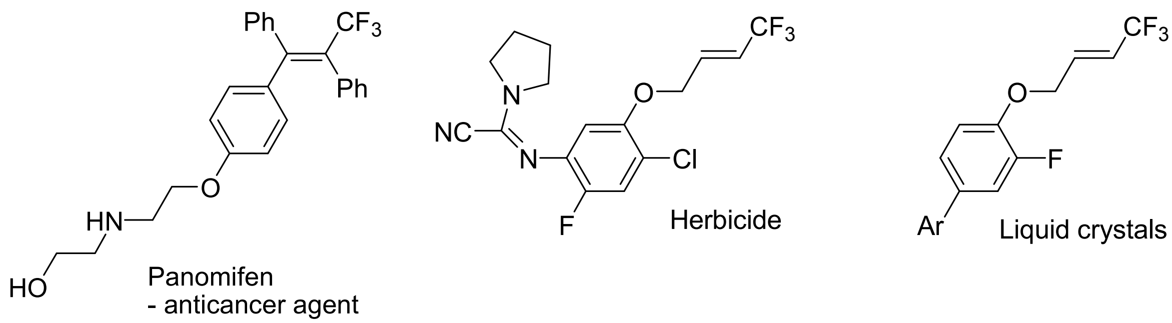
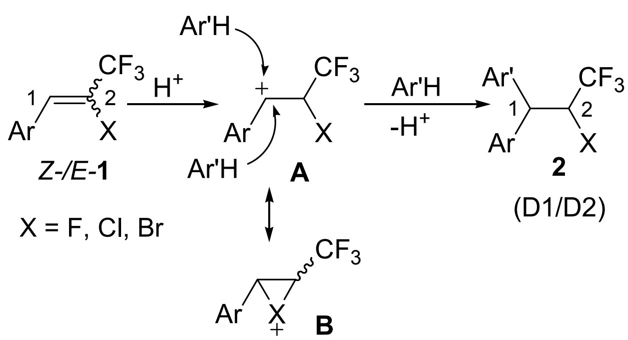


Figure 1. Some examples of practically valuable CF_3-alkenes.

Synthesis of CF_3-alkenes is an important target in organic chemistry.[2] These alkenes take part in many various transformations with nucleophiles.[3] They react with aryl halides,[4] organosilanes,[5] organoboron[6] and organolithium compounds.[7] CF_3-alkenes participate in reactions with enamines,[8] enolates,[9] terminal alkynes.[10] They undergo oxidative cyclization with aldehydes,[11] and may be involved in many other reactions.[12] CF_3-Alkenes are valuable monomers and they are used in chemistry of polymers.[13] But up-to date, there are only two examples of participation of CF_3-substituted alkenes in Friedel-Crafts process under the superacidic activation.[14] Analogous reactions with CF_3-alkenes having additional halogens at the C=C bond are unknown up to the moment. The presence of a halogen atom (F, Cl, Br) in the structure of cationic intermediates may stabilize these species via the formation of cyclic halonium cations. These halonium ions are postulated as intermediates of electrophilic reactions of alkenes.[15] The stability of halonium ions is increased from light to heavy atoms. Iodonium and bromonium salts were isolated, but generation of fluoronium ions was shown only recently.[16]

Based on our preliminary communication[17] and recent publications on reactions of CF_3-alkynes,[18] CF_3CO-alkenes,[19] and CF_3-allyl alcohols[20] in acids, we undertook special study on reactions of CF_3-styrenes bearing at the double bond additional halogen atom under superelectrophilic activation.

The main goals of this work are: a) investigation of protonation of 1-aryl-2-halogeno-3,3,3-trifluoropropenes (2-halogeno-2-CF_3-styrenes) in superacids CF_3SO_3H (triflic acid) and FSO_3H (fluorosulfonic acid); b) theoretical (DFT) and experimental spectral (NMR) study of the formed carbocations; c) Friedel-Crafts alkylation of arenes and study of synthetic potential of the method. Also, one of the key point of this study is to check a stability of C^2–X (X = F, Cl, Br) bond under superacidic conditions. Usually this kind of carbon-halogen bond is easily cleaved in superacids.[21]



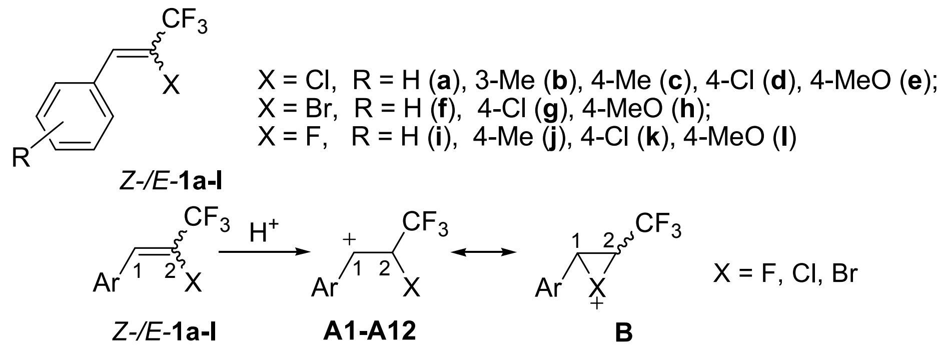
Scheme 1. Protonation of **1** leading to cations **A**, **B** followed by reaction with arenes

Protonation of styrenes **1** should proceed exclusively at C^2 carbon giving rise to benzyl cations **A**, due to the acceptor properties of CF_3 group. Cations **A** may exist in form of halonium ions **B** (Scheme 1). These species **A** and **B** may participate in Friedel-Crafts alkylation of arenes affording CF_3-diarylethanes **2**. The reaction of "closed" cations **B** with arenes may proceed stereoselectively (in S_N2 manner), opposite to the reactivity of "linear" cations **A**, for which a higher loss of stereoselectivity may be observed due to attack of arene nucleophile from both sides of these species. In the latter case the reaction should be less stereoselective and the formation of diastereomeric (D1/D2) mixtures of **2** should be observed.

RESULTS AND DISCUSSION

Initial 1-aryl-2-halogeno-3,3,3-trifluoropropenes **1a-l** were obtained by reaction of aryl aldehydes with 1,1,1-trifluoro-2,2,2-trihaloethanes.[2a-c] To estimate electronic properties of reaction intermediates, we performed DFT calculations (B3LYP) of cations **A**, **B**, derived from styrenes **1** (Table 1). Charge distribution, contribution of atomic orbital into molecular orbital, and global electrophilicity indices ω[22] were calculated. In "open form" cations **A1-A12** atom C^1 bears a positive charge (0.02-0.12 e) and has large LUMO contribution (25.9-48.1%) (Table 1). These data indicate a coincidence of charge and orbital control in reactivity of this carbon, as an electrophilic center. Calculations of "closed" halonium ions **B1**, **B6**, **B8**, **B9** (Table 1) showed that chloro (**B1**) and fluoro (**B9**) substituted cations were extremely unstable they corresponded to transition states (one imaginary frequency), rather than local minimums. Bromo substituted species **B6**, **B8** are relatively stable. Comparison of the charge on C^1 for pairs of cations **A1-B1**, **A6-B6**, **A8-B8**, **A9-B9** reveals that species **A** have a greater positive charge on this carbon than corresponding cations **B**, except for the fluoro-substituted pair **A9-B9**. Also, in ions **B1**, **B6**, **B8**, **B9** atom C^1 gives a large contribution to LUMO (up to 50 %). Halogen atoms X (F, Cl, Br) have a greater positive charge and LUMO coefficients in cations **B** than in species **A**. However, for all bromo derivatives participation of halogen in cation stabilization is much more considerable than for chloro and fluoro species according to LUMO distribution. Comparison of electrophilicity indices reveals that cations **A** have higher values of ω (5.4-6.7 eV) than the corresponding halonium ions **B** (3.9-4.5 eV). Thus, species **A** should be more reactive than **B**.

Table 1. Selected characteristics of cations A1-A12, B1, B6, B8, B9 (DFT calculations)



cation	X	R in Ar	E_{HOMO}, eV	E_{LUMO}, eV	ω,[a] eV	q(C^1),[b]	q(C^2),[b]	q(X)[b]	k(C^1) $_{LUMO}$,[c] %	k(X) $_{LUMO}$,[c] %
A1	Cl	H	-8.67	-5.12	6.7	0.12	-0.32	0.06	48.1	4.4
A2	Cl	3-Me	-8.34	-5.06	6.8	0.12	-0.32	0.05	29.7	4.2
A3	Cl	4-Me	-8.63	-4.91	6.1	0.09	-0.32	0.04	27.0	5.4
A4	Cl	4-Cl	-8.80	-5.11	6.6	0.10	-0.32	0.05	29.1	4.5
A5	Cl	4-MeO	-8.37	-4.54	5.4	0.03	-0.31	0.02	28.7	5.7
A6	Br	H	-8.60	-5.06	6.6	0.11	-0.38	0.11	34.7	16.7
A7	Br	4-Cl	-8.58	-5.07	6.6	0.09	-0.38	0.15	30.9	13.5
A8	Br	4-MeO	-8.21	-4.54	5.5	0.03	-0.37	0.11	30.4	14.6
A9	F	H	-8.73	-5.18	6.8	0.12	0.11	-0.36	25.9	0.7
A10	F	4-Me	8.68	-4.94	6.2	0.08	0.11	-0.36	22.7	0.6
A11	F	4-Cl	-8.92	-5.16	6.6	0.10	0.11	-0.36	23.1	0.7
A12	F	4-MeO	-8.48	-4.54	5.4	0.02	0.12	-0.36	28.1	1.2
B1	Cl	H	-8.05	-4.00	4.5	0.02	-0.24	0.32	48.5	3.5
B6	Br	H	-7.94	-3.72	4.0	-0.10	-0.30	0.55	50.0	12.9
B8	Br	4-MeO	-7.32	-3.56	3.9	-0.11	-0.30	0.53	42.1	18.4
B9	F	H	-7.96	-3.92	4.4	0.19	0.19	-0.20	17.2	15.0

[a]Global electrophilicity index $\omega = (E_{HOMO} + E_{LUMO})^2/8(E_{LUMO} - E_{HOMO})$; [b]Natural charges; [c]Contribution of atomic orbitals into the molecular orbital.

Calculated geometries of cations **A1-A12** (see SI) show that dihedral angles θ between planes including atoms $C_{ipso\text{-}Ar}$–C^1–C^2–X(F, Cl, Br) are ~108-110° for chloro-substituted (X = Cl) species **A1**-**A5** and ~104-105° for bromo-substituted (X = Br) cations **A6-A8** (see selected examples in Figure 2). These angles indicate that halogen atom is located above the plane including aryl ring and carbocationic center C^1, revealing that bond C^2–X is almost perpendicular to this plane. This orientation of halogen X should be the most favorable for partial positive charge delocalization from C^1 to atom X. Contrary to that, in fluoro-substituted (X = F) cations **A9-A12** the angle θ is ~147-153° (see SI and **A9** in Figure 3). So, for these species fluorine X lies almost in the same plane containing aryl ring and C^1 atom. That reveals the minimal possibilities for charge delocalization from C^1 to fluorine atom in **A9-A12**. Thus, calculated geometries of **A1-A12** show that halogen atom X in chloro and bromo substituted ions **A1-A8** may participate in positive charge delocalization, leading to the formation of halonium cations **B**, that does not take place for fluorinated species **A9-A12**.

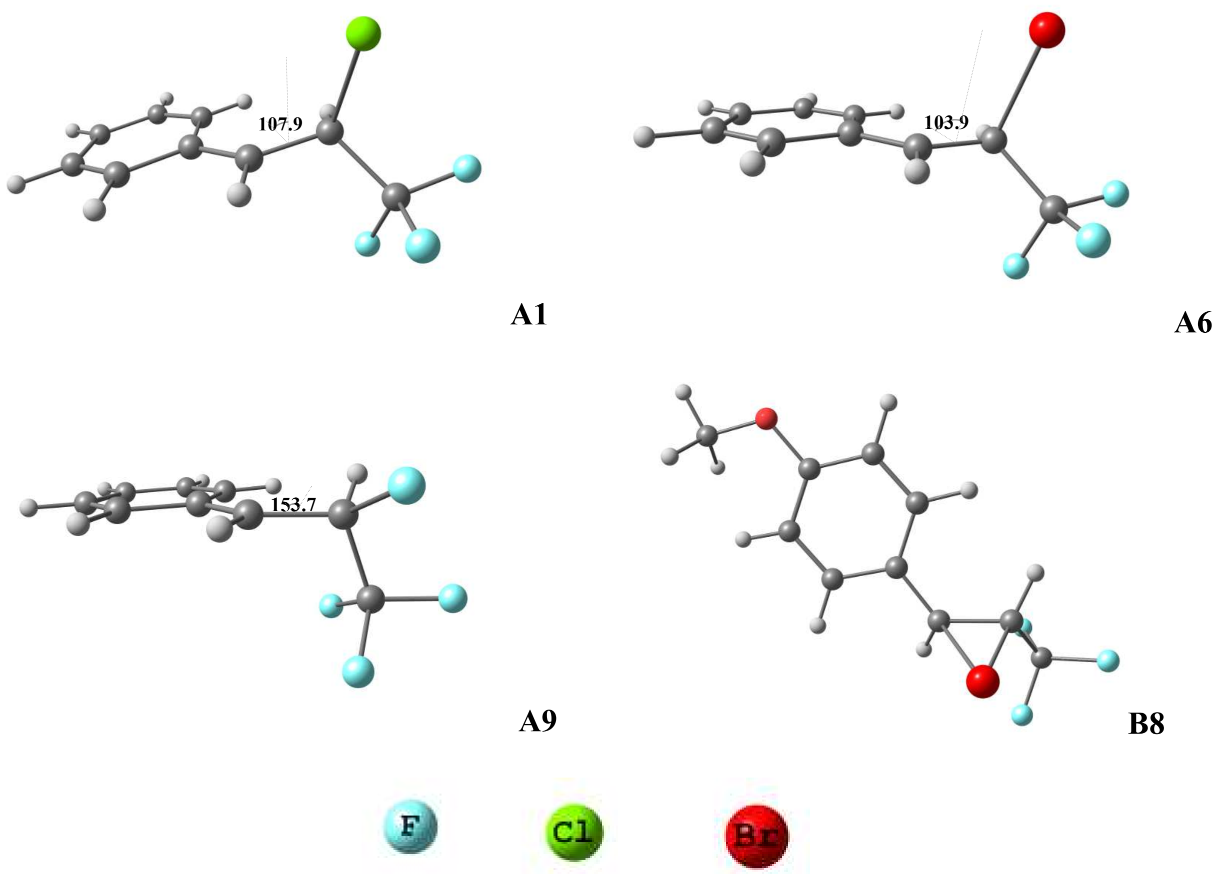


Figure 2. Calculated geometries of the selected species **A1**, **A6**, **A9**, **B8** (dihedral angle θ between planes including atoms $C_{ipso\text{-Ar}}$–C^1–C^2–X(F, Cl, Br) is depicted for **A1**, **A6**, **A9**).

Then we undertook NMR study of protonation of styrenes **1a-l** in the superacids CF_3SO_3H and FSO_3H. Accordingly to ^{1}H NMR, no protonation occurs below -20 °C for **1a-l** in these superacids. But at higher temperatures between -20 and 20 °C protonation of the double bond takes place and formation of oligomers is observed (see below). Among all studied alkenes **1a-l**, we succeeded to catch intermediate cation only in the case of methoxyphenyl substituted alkene **1h**, which gave protonated species in FSO_3H at 0 °C (see Figure 3, and other spectral data in Experimental section and SI). The assignment of signals in proton and carbon spectra of this species was done based on ^1H–^{13}C HSQC spectrum (see SI).

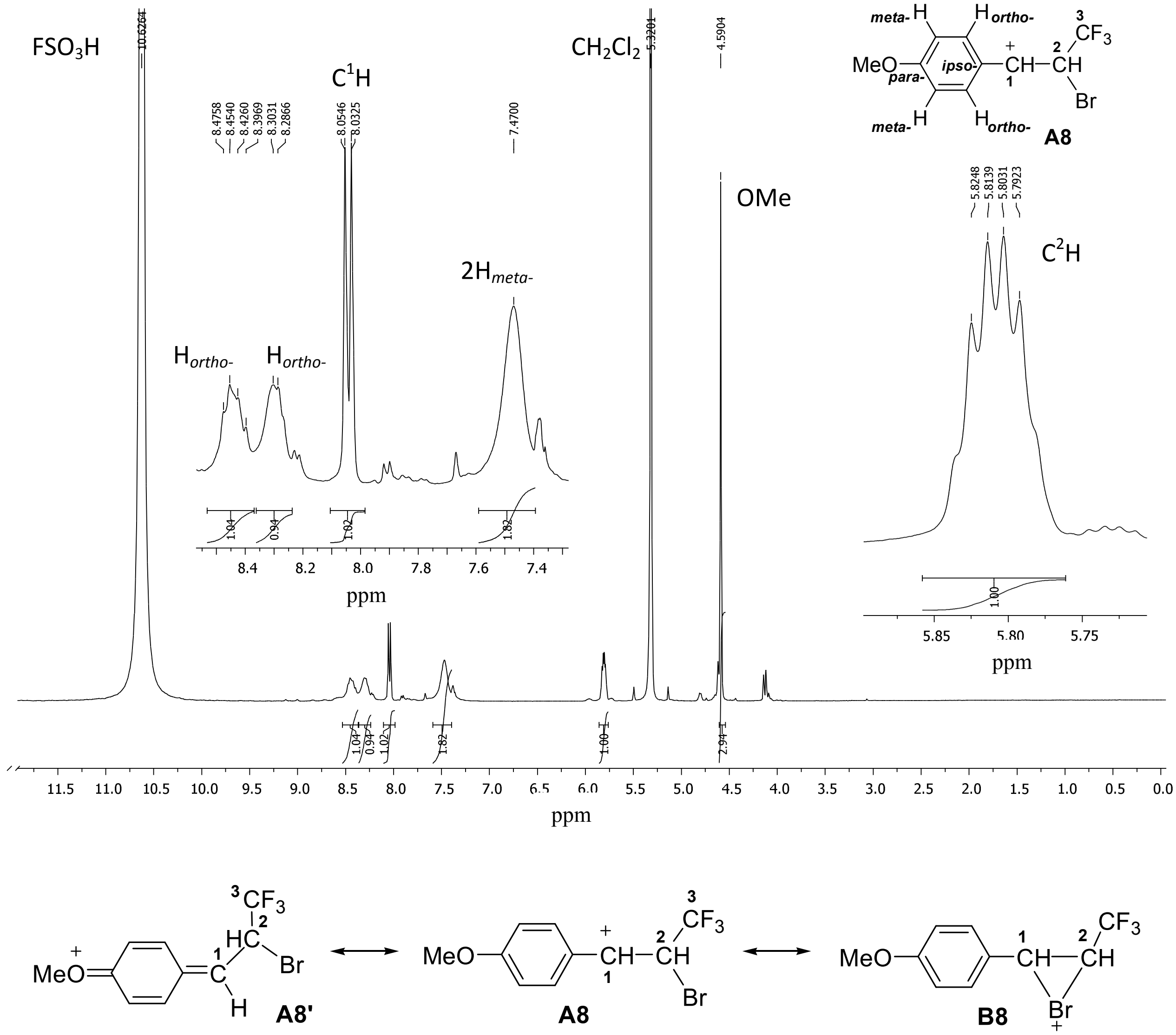


Figure 3. ^1H NMR spectrum of **A8** in FSO_3H at 0°C (500 MHz, CH_2Cl_2 is added as internal standard).

A new signal appeared in the ^{1}H NMR spectrum of styrene **1h** under protonation (doublet of quartets at δ 5.81 ppm) (Figure 3). This signal corresponds to new proton attached to the carbon C^2. The corresponding spin-spin interactions are detected in the signal of proton at C^1 carbon in ^{1}H NMR (Figure 3) and in the signal of CF_3 group in ^{19}F NMR (see Experimental section and SI). This protonated species, most probably, may be described as cation **A8** (see Scheme in Figure 3). Accordingly to ^{1}H and ^{13}C NMR data, $C_{ipso\text{-}Ar}$–C^1 bond has restricted rotation leading to broadening and nonequivalence of the signals of aromatic *ortho- and meta*-protons and carbons (Figure 3, and SI), due to significant contribution of mesomeric form **A8′**. One more evidence for this mesomeric form is a significant down-field shift of $C_{para\text{-}}$ at 189.5 ppm in ^{13}C NMR (Experimental section, SI), revealing a substantial positive charge delocalization into *p*-methoxyphenyl ring.

But, more striking spectral behavior is shown by the position of the signal of carbocation center $^{+}C^1$, which is very much up-field shifted to 164.5 ppm in ^{13}C NMR (see Experimental Section and SI). Similar signal of other benzyl cations is usually registered in the region ~182-270 ppm (Figure 4). That means that there is an additional structural possibility for charge delocalization in cation **A8**. Most probably, this possibility may come from bromine atom resulting in the formation of halonium ion **B8** (see calculated structure in Figure 2).

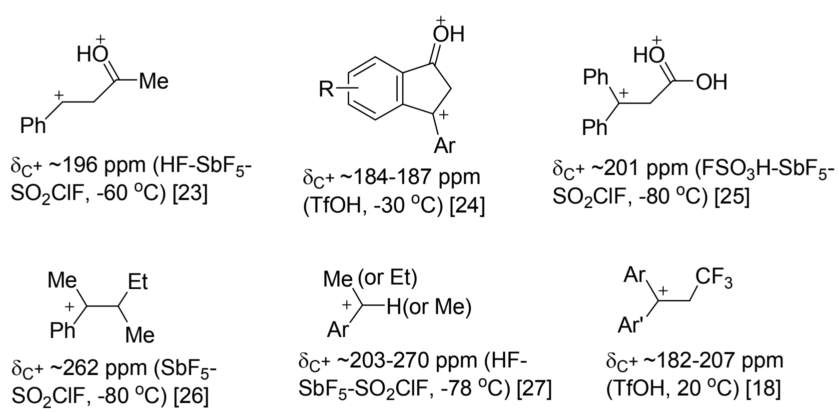


Figure 4. ^{13}C NMR chemical shifts of carbocation center of some benzyl cations ([18, 23-27]).

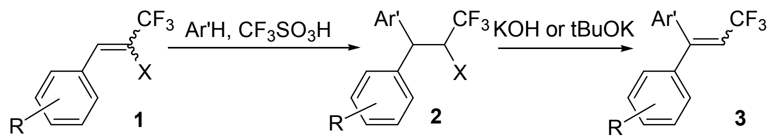
Thus, NMR data on the protonation of alkene **1h** in the superacid FSO_3H clearly demonstrates that the formed species **A8** may exist at least in two additional mesomeric forms **A8′** and **B8**. In other words, the structure of protonated form of **1h** may be described as a superposition of these mesomeric forms having different contributions. And once again, nonequivalence and broadness of proton and carbon signals in NMR spectra reflect the complex structure of this protonated species, which is hard to cauch.

As it was mentioned above, the formation of oligomers was detected on protonation of styrenes **1** in the superacids CF_3SO_3H and FSO_3H. We carried out preparative reactions and isolated these oligomers obtained from compounds **1b**,**e**,**f** in CF_3SO_3H at room temperature for 0.5 h. According to MALDI-MS data (see SI) the oligomers are products of cationic polymerization, consisting of up to 14 subunits of starting styrenes **1b**,**e**,**f**.

Then we studied Friedel-Crafts alkylation of arenes with styrenes **1** in CF_3SO_3H. Table 2 contains data on these reactions of chloro **1a-e**, bromo **1f-h**, and fluoro **1i-l** substituted styrenes. The reaction leads to products of hydroarylation of double bond, 1,1-diaryl-2-halogeno-3,3,3-trifluoropropanes *Z-/E-***2**. It should be noted that no reaction is observed in trifluoroacetic acid CF_3CO_2H, which is too weak to protonate such deactivated carbon-carbon double bond in **1**. Methoxyphenyl substituted compounds **1e**,**h**,**l** were protonated in sulfuric acid, they even interacted with benzene, but gave reaction products in much lower yields, compared to CF_3SO_3H.

Various arenes may be involved in the reaction with alkenes **1** in CF_3SO_3H: benzene, toluene (methylbenzene), isomeric xylenes (dimethylbenzenes), pseudocumene (1,2,4-trimethylbenzene), anisole (methoxybenzene), veratrole (1,2-dimethoxybenzene), and such deactivated arene as 1,2-dichlorobenzene (Table 2). This reaction affords the target CF_3-propanes **2** in good yields. The reaction was very regioselective relatively to aromatic substrates. Thus, the carbocation formed attacked only the *para*-position of the substituted arenes (see reactions with toluene, *o*-xylene, anisole, and veratrol in Table 2).

Table 2. Hydroarylation of Styrenes 1 in CF_3SO_3H, and Dehydrohalogenation of 2

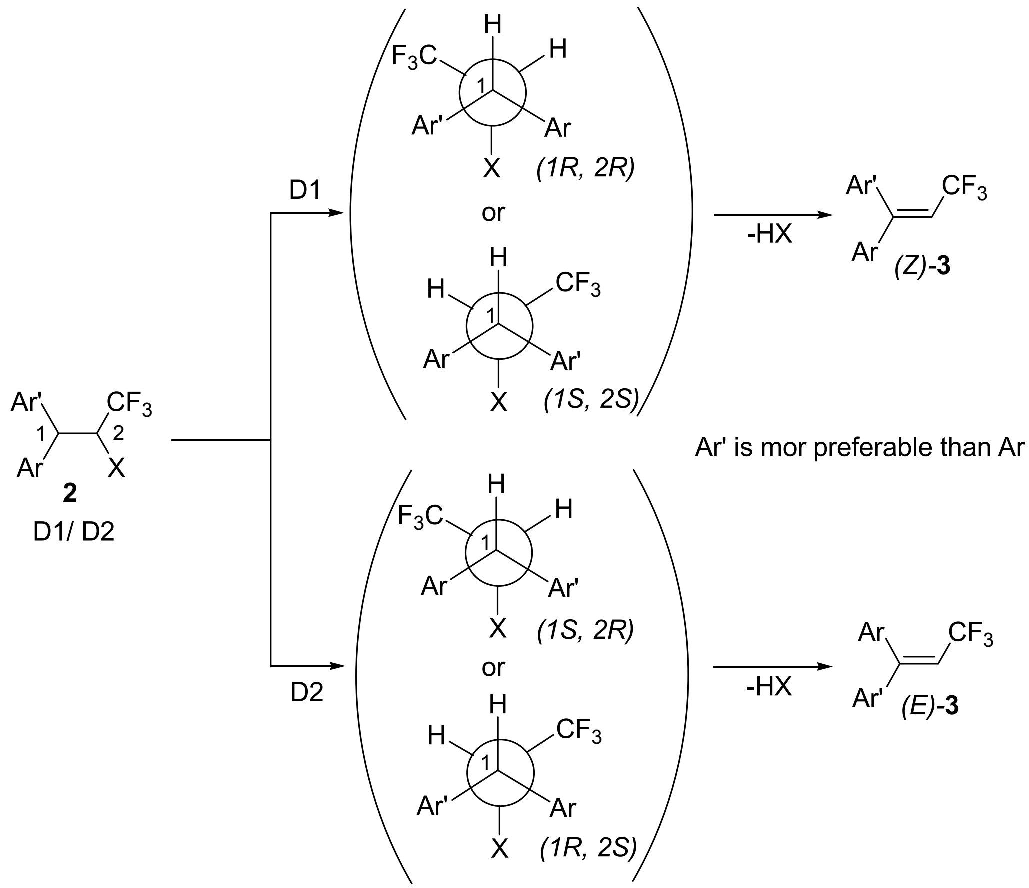


Entry	*Z/E*-ratio for **1**	X	R in Ar	Ar′H[a]	Ar′ for **2**, **3**	**2** (yield, %)	**3** (yield, %)	D1/D2 for **2** and *Z/E* for **3**
1	**1a** (83 : 17)	Cl	H	benzene [b]	Ph	**2a** (86)	**3a** (89)	–
2	**1a** (83 : 17)	Cl	H	toluene [c]	4-MeC_6H_4	**2b** (91)	**3b** (72)	37 : 63
3	**1a** (83 : 17)	Cl	H	*o*-xylene [c]	3,4-$Me_2C_6H_3$	**2c** (91)	**3c** (87)	53 : 47
4	**1a** (83 : 17)	Cl	H	*m*-xylene [c]	2,4-$Me_2C_6H_3$	**2d** (66)	**3d** (85)	29 : 71
5	**1a** (83 : 17)	Cl	H	*p*-xylene [c]	2,5-$Me_2C_6H_3$	**2e** (89)	**3e** (79)	67: 33
6	**1a** (83 : 17)	Cl	H	pseudocumene [c]	2,4,5-$Me_3C_6H_2$ 2,3,5- $Me_3C_6H_2$	**2f** (73) **2g** (14)	**3f** (74) **3g** (15)	53: 47 50: 50
7	**1a** (83 : 17)	Cl	H	1,2–dichlorobenzene [d]	3,4-$Cl_2C_6H_3$	**2h** (22)	**3h** (89)	83 :17
8	**1a** (83 : 17)	Cl	H	anisole [c]	4-$MeOC_6H_4$	**2i** (70)	**3i** (87)	42: 58
9	**1a** (83 : 17)	Cl	H	veratrole [d]	3,4-$(MeO)_2C_6H_3$	**2j** (43)	**3j** (86)	40: 60
10	**1b** (83 : 17)	Cl	3-Me	benzene [b]	Ph	**2k** (78)	**3k** (85)	77 : 23
11	**1c** (86 : 14)	Cl	4-Me	benzene [e]	Ph	**2b** (96)	**3b** (87)	71 : 29
12	**1c** (86 : 14)	Cl	4-Me	anisole [e]	4-$MeOC_6H_4$	**2l** (66)	**3l** (81)	67 : 33
13	**1d** (75 : 25)	Cl	4-Cl	benzene [f]	Ph	**2m** (91)	**3m** (85)	75 :25
14	**1d** (75 : 25)	Cl	4-Cl	anisole [e]	4-$MeOC_6H_4$	**2n** (81)	**3n** (85)	63 :37
15	**1d** (75 : 25)	Cl	4-Cl	1,2–dichlorobenzene [d]	3,4-$Cl_2C_6H_3$	**2o** (91)	**3o** (85)	67 : 33
16	**1e** (91 : 9)	Cl	4-MeO	benzene [d]	Ph	**2i** (89)	**3i** (94)	83 : 17
17	**1e** (91 : 9)	Cl	4-MeO	anisole [d]	4-$MeOC_6H_4$	**2p** (89)	**3p** (91)	–
18	**1e** (91 : 9)	Cl	4-MeO	veratrole [d]	3,4-$(MeO)_2C_6H_3$	**2q** (27)	**3q** (96)	52 : 48
19	**1f** (89 : 11)	Br	H	benzene [b]	Ph	**2r** (88)	**3a** (89)	–
20	**1f** (89 : 11)	Br	H	p-xylene [c]	2,5-$Me_2C_6H_3$	**2s** (67)	**3e** (68)	35: 65
21	**1f** (89 : 11)	Br	H	anisole [c]	4-$MeOC_6H_4$	**2t** (95)	**3i** (87)	71 : 29
22	**1f** (89 : 11)	Br	H	veratrole [c]	3,4-$(MeO)_2C_6H_3$	**2u** (80)	**3a** (90)	61 : 39
23	**1g** (75 : 25)	Br	4-Cl	benzene [b]	Ph	**2v** (76)	**3m** (95)	66 : 34
24	**1g** (75 : 25)	Br	4-Cl	anisole [b]	4-$MeOC_6H_4$	**2w** (52)	**3n** (95)	63 : 37
25	**1h** (91 : 9)	Br	4-MeO	benzene [d]	Ph	**2t** (54)	**3i** (87)	53 : 47
26	**1h** (91 : 9)	Br	4-MeO	anisole[c]	4-$MeOC_6H_4$	**2x** (91)	**3p** (81)	–
27	**1h** (91 : 9)	Br	4-MeO	veratrole [d]	3,4-$(MeO)_2C_6H_3$	**2y** (46)	**3q** (96)	52 : 48
28	**1i** (97 : 3)	F	H	benzene [b]	Ph	**2z** (78)	**3a** (90)	–
29	**1j** (97 : 3)	F	4-Me	benzene [c]	Ph	**2za** (67)	**3b** (88)	59: 41
30	**1k** (97 : 3)	F	4-Cl	benzene [f]	Ph	**2zb** (92)	**3m** (92)	56: 44
31	**1k** (97 : 3)	F	4-Cl	anisole [f]	4-$MeOC_6H_4$	**2zc** (20)	**3n** (82)	64 : 36
32	**1l** (97 : 3)	F	4-MeO	benzene [d]	Ph	**2zd** (90)	**3i** (93)	33 : 67
33	**1l** (97 : 3)	F	4-MeO	anisole [d]	4-$MeOC_6H_4$	**2ze** (58)	**3p** (89)	–
34	**1l** (97 : 3)	F	4-MeO	veratrole [e]	3,4-$(MeO)_2C_6H_3$	**2zf** (28)	**3q** (92)	51 : 49

[a]Molar ratio **1** : arene 1 : 5, for benzene 1 : 17. [b]Room temperature, 1 h. [c]-10 °C, 3 h, with CH_2Cl_2 as co-solvent. [d]Room temperature, 0.5 h. [e]-10 °C, 0.5 h, with CH_2Cl_2 as co-solvent. [f]60 °C, 1 h.

The stereochemical result of the reaction is very important. This data gives us the information about participation of a halogen X in stabilization of formed benzylic carbocations. In all cases the formation of inseparable mixtures of two diastereomers of **2** (D1/D2) in a various ratio was observed. Moreover the ratio of D1 and D2 differs from the *Z/E*-ratio of staring alkenes **1**. These diastereomers **2** have different *(R)*-, *(S)*- configurations of atoms C^1 and C^2: D1 (*1RS*, *2RS*) and D2 (*1SR*, *2RS*). In all ^{1}H, ^{13}C, and ^{19}F NMR spectra, two sets of signals of each diastereomer **2** were detected (see SI). The exact structure of these diastereomers can not be determined using NMR. However, we found simple way to resolve this problem. We carried out dehydrohalogenation of compounds **2** to give alkenes **3**, as inseparable mixture of *Z/E*-isomers, by treatment with a base (KOH or *t*-BuOK, Table 2). Alkenes **3** are structural analogs of Panomifen, which is an antitumor drug (Figure 1). Therefore, synthesis of alkenes **3** is of significant practical value.[28]

The *Z/E*-ratios for the alkenes **3** was the same as the D1/D2 ratios for their precursors **2** in cases of chloro and bromo substituted derivatives. Based on these stereochemical data, one can conclude that compounds **3** are formed from **2** in E2 elimination way. Diastereomers D1(*1RS*,*2RS*) gave *Z*-alkenes **3**, and diastereomers D2 (*1SR*,*2RS*) yielded *E*-isomers **3**, as it is presented in Scheme 2 with Newman projections. The configuration of the *Z*- and *E*-isomers of **3** can be figured out by means of ^{1}H NMR. The signal of vinyl proton in *E*-isomers **3** is low field shifted compared to the same signal in *Z*-isomer.[18] Based on these spectral regularity, we could elucidate the stereochemistry of *Z/E*-alkenes **3** and, consequently, resolve the structures of diastereomers **2**, D1 and D2.

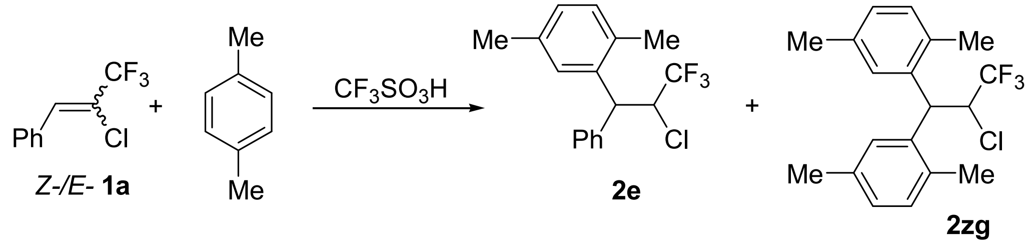


Scheme 2. Newman Projections of 2 and Stereochemistry of Compounds 2 and 3.

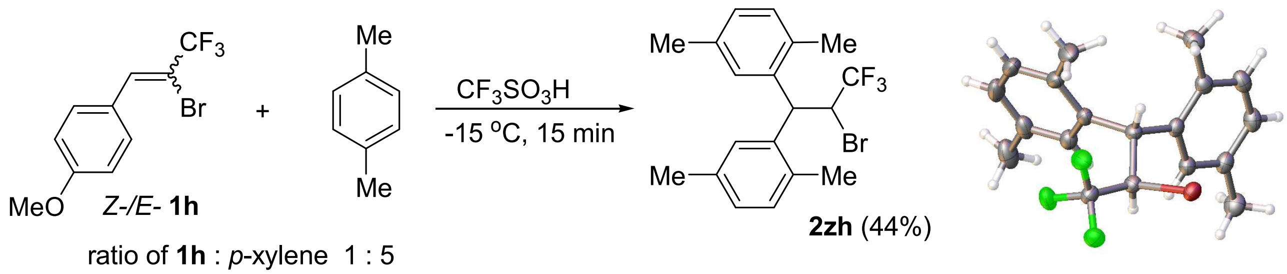
Some moments should be pointed out concerning the elimination of HX from compounds **2.** Dehydrobromination proceeded smoothly with KOH in ethanol even at room temperature. In the case of chloro derivatives **2a-q**, it is necessary to use KOH under reflux in ethanol to get alkenes **3a-q** (see Experimental section). Dehydrofluorination needs harder conditions (KOH, reflux, ethanol, 20 h). The elimination of HF in these conditions is not stereoselective and give alkene **3** with a *Z/E*-ratio of 1:1, in spite of the ratio of diastereomers **2** being initially not 1 : 1 (Table 3). This reveals that, due to the strong acceptor character of the CF_3 and F groups, elimination of HF from compounds **2**, most probably, proceeds in E1cb way, rather than an E2 one (contrary to substances **2** with X = Cl, Br). It was found that dehydrofluorination of **2z-zf** could be done stereoselectively with *t*-BuOK in THF, yielding the alkenes **3** with *Z/E*-ratios corresponding to that of D1/D2 for **2z-zf**.

We observed also some additional processes during this type of Friedel-Crafts alkylation of arenes. In some cases the reaction can be complicated by exchange of aryl groups. Thus, the reaction of **1a** with such strong π-nucleophile as *p*-xylene gave at room temperature, apart from target product **2e,** the compound **2zg** (entries 2, 3, Table 3). The formation of **2zg** can be explained by protonation of aryl group or protonation of $C^1–C_{Ar}$ bond under superacidic conditions followed by elimination of arene molecule and formation of the corresponding benzyl cation reacting with excess of *p*-xylene. There are two crucial points for such aryl exchange. These are reaction temperature and ratio of starting styrene **1** and arene. When ratio of **1** : arene is 1 : 1, the oligomers are formed only, due to concurrent reaction of cationic polymerization of styrenes **1** (Table 3, entry 1, and see above MALDI-MS data on oligomerization). In excess of *p*-xylene (ratios of **1** : arene 1 : 5) the oligomerization of **1** is completely suppressed (Table 3, entry 2). So, to achieve hydroarylation of alkenes **1** we used excess of arenes as it is indicated in Table 2. Lowering reaction temperature also allows to avoid aryl group exchange (Table 3, entries 4, 5). Reactions of alkenes **1** with good π-nucleophiles (xylenes, anisol, veratrol) were mainly conducted at -10 °C to avoid formation of byproducts (see Table 2). But, *p*-methoxyphenyl substituted alkene **1h** in reaction with *p*-xylene gave only exchange product **2zh** even at -15 °C (Scheme 3), due to more efficient substitution of *p*-methoxyphenyl fragment. Recently we described similar aryl exchange group process and its suppression for hydroarylation of cinnamides in superacids.[29]

Table 3. Exchange of Aryl Group in Reaction of 1a with *p*-Xylene

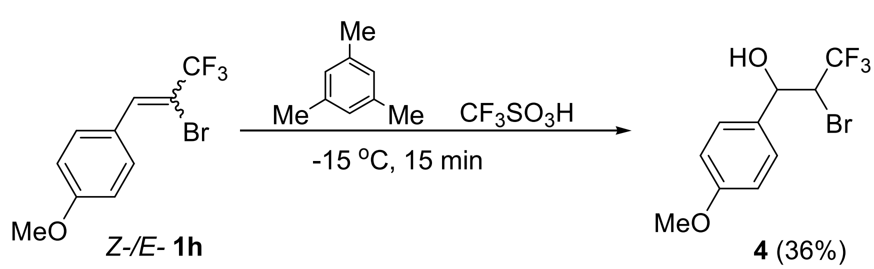


entry	reaction condition			reaction products	
	ratio of **1a** : ***p*-xylene**	temperature, °C	time, h	ratio of **2e** : **2zg**	whole yield of **2e** : **2zg** , %
1	1 : 1	r.t.	0.5	quantitative formation of oligomers	
2	1 : 5	r.t.	0.5	9 : 1	90
3	1 : 5	r.t.	5	1 : 1.4	37
4	1 : 5	-10	0.25	1 : 0	60
5	1 : 5	-10	3	1 : 0	89



Scheme 3. Aryl exchange in the reaction of 1h with *p*-xylene. Molecular structures of 2zh (ellipsoid contours of probability levels are 50 %).

Polymethyl substituted arenes, mesitylene and durene, did not participate in the reaction with styrene **1** due to higher steric demand of carbocations formed by protonation of **1**. At room temperature styrenes **1** under the reaction conditions in the presence of mesitylene and durene formed only oligomers. At lower temperature (-15 °C) the generated cation **A8** from **1h** did not react with mesitylene, but was transformed into alcohol **4** (Scheme 4) after quench of the reaction mixture with water (see Experimental).



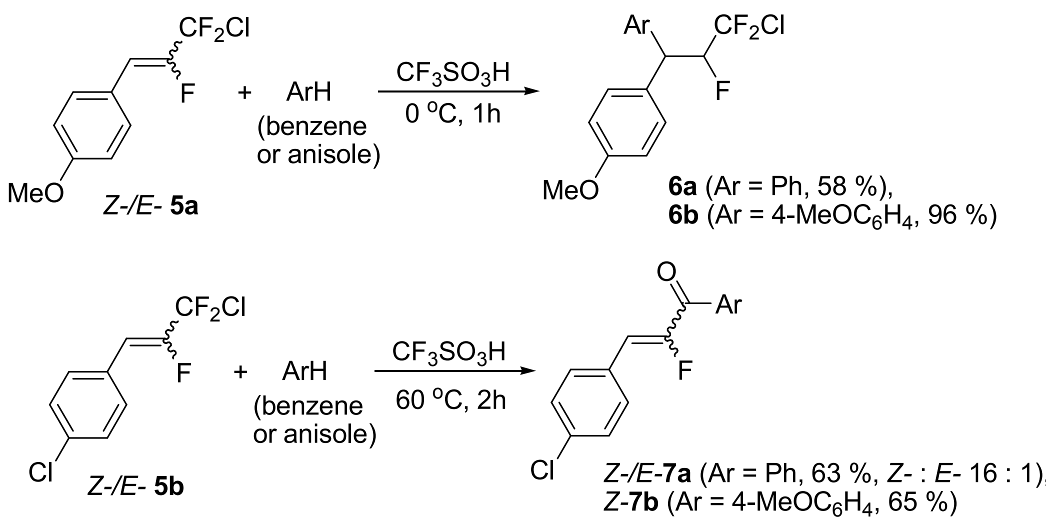
Scheme 4. Transformation of 1h into Alcohol 4

Summarizing this part of the study (Tables 2, 3, Schemes 3, 4), some features of this reaction should be pointed out. The reaction is very sensitive to the halogen atom X on the C=C bond and to substituents on the arene ring in compounds **1**. All bromo substituted (X = Br) compounds **1f-h** are easily protonated in CF_3SO_3H at -10 °C and smoothly react with arenes (entries 19-27, Table 2). Substrates **1i-l**, having stronger electron acceptors X = Cl, F, need room temperature or 60 °C to react with arenes (entries 1-18, 28-34, Table 2). Apart from that, alkenes **1d** and **1k,** with X = Cl and F, respectively, bearing an acceptor *para*-chlorophenyl ring, are hardly protonated in CF_3SO_3H. Compounds **1d** and **1k** react with benzene at higher temperature of 60 °C (entries 13, 30, 31, and Table 2). Other alkenes **1** containing electron donating substituents (Me, OMe) on aryl ring react smoothly at -10 °C or room temperature (Tables 2). Also, it should be mentioned that C^2–X (X = F, Cl, Br) bond in compounds **2** is stable under superacidic reaction conditions, due to the electron withdrawing influence of the neighboring CF_3 group, despite of many examples of cleavage of this kind of bond in superacids.[21]

In many cases the hydroarylation of double bond in **1** goes very stereoselectively leading mainly to preferable formation of one of the diastereomers D1 or D2 (see D1/D2 ratios in Table 2). The ratio of D1/D2, most probably, strongly depends on spatial factors. Despite the absence of high stereoselectivity in this reaction, the data on the diastereomeric ratios for compounds **2** shed light on the reactivity of cations **A** and **B** (Scheme 1). Thus, the stereoselectivity is reduced for fluoroalkenes **1i-l** (X = F). Starting from alkenes **1j-l** having *Z/E-* ratio 97 : 3, the reaction led to compounds **2z-zf** with D1/D2 ratios from 33 : 67 to 64 : 36 (Table 2). In this case a loss of stereoselectivity reveals that a cyclic fluoronium ion **B** cannot be formed, and the stereocontrol could come only from a cation **A**. For bromo- (X = Br) and chloro- (X = Cl) alkenes **1** the formation of cyclic ions **B** is more probable.

We also tested activation of styrenes **5a,b** in CF_3SO_3H bearing at the double bond fluorine and CF_2Cl group and the subsequent reaction with arenes (Scheme 5). Activated by donating methoxyphenyl group, compound **5a** is easily protonated at 0 °C and give the corresponding hydroarylation products **6a,b** in reaction with benzene and anisole respectively. The key point is a stability of C–Cl bond in compounds **5a,b** under the superacidic conditions at 0 °C.

On the other hand, deactivated C=C bond in *para*-chloro substituted styrene **5b** is not protonated in CF_3SO_3H even at elevated temperature 60 °C. This styrene reacts only in a way of Friedel-Crafts reaction at C–Cl bond with arenes, followed by hydrolysis of two fluorine atoms under quench with water. Fluorinated chalcones **7a**,**b** are formed as a result of this reaction sequence. Reaction is highly stereoselective, leading predominantly to *Z*-isomer of **7**. *E/Z*-Stereochemistry of compounds **7a**,**b** was determined by $^1H–^{19}F$ NOESY correlation between the vinyl proton and *ortho*-protons on 3-aryl ring (see SI). Such 2-fluorochalcones are hardly available compounds, they are in great interest due to biological activity of chalcone derivatives, and there are just a few published methods for their synthesis.[30]



Scheme 5. Reactions of Styrenes *E-/Z*-5a,b with Arenes.

CONCLUSIONS

We have shown that 2-halogeno-2-CF_3 styrenes in Friedel-Crafts reaction with arenes in CF_3SO_3H gave rise to 1,1-diaryl-2-halogeno-3,3,3-trifluoro propanes. This is a simple and efficient synthetic metod for hydroarylation of double bond of such CF_3-styrenes. The intermediate cationic species of this reaction were studied by means of NMR and DFT calculations. Dehydrohalogenation of 1,1-diaryl-2-halogeno-3,3,3-trifluoro propanes under mild conditions resulted in the formation of 1,1-diaryl-3,3,3-trifluoro propenes.

EXPERIMENTAL SECTION

General information

NMR spectra were recorded on spectrometer (at 500 MHz, at 125 MHz, and at 470 MHz for ^{1}H, ^{13}C and ^{19}F NMR spectra respectively) and on spectrometer (at 400, 100, and 376 MHz for ^{1}H, ^{19}F and ^{13}C NMR spectra respectively) using $CDCl_3$ as a solvent or FSO_3H and CF_3SO_3H to generate protonated forms of styrenes **1** with CH_2Cl_2 as internal standard. The ^{1}H and ^{13}C spectra were calibrated using the residual signals of nondeuterated solvent as internal reference. The ^{19}F spectra are referenced through the solvent lock (2H) signal according to IUPAC recommended secondary referencing method and the manufacturer's protocols. ^{19}F NMR shifts are given relatively to the signal of $CFCl_3$ (δ 0.0 ppm). 2D NOESY and HSQC spectra were taken. High resolution mass spectra (HRMS) were carried out at MALDI-MS spectrometer with 9.4 Tesla superconducting magnet equipped with a UV laser (Nd) in the positive ion mode or at instrument for HRMS-ESI-QTOF. Chromato-mass-spectrometry data were obtained at system with HP-5MS capillary column (30 m × 0.25 mm), thickness of the stationary phase 0.25 μm. Column chromatography was performed on silica gel 40-63 μm. Purity of compounds was monitored by TLC.

X-ray analysis. A suitable crystals were selected and studied on the diffractometer for X-ray analysis. The crystals were kept at 100(2) K during data collection. Using Olex2[31] the structure was solved with the ShelXS[32] structure solution program using Direct Methods and refined with the ShelXL refinement package using Least Squares minimization. CCDC 1452574 – (**2zh**) contains the supplementary crystallographic data, which can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.htmL or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.)+44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk.

DFT calculations. All computations were carried out at the DFT/HF hybrid level of theory using 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.[33] The geometries optimization were 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. Solvent-phase calculations used the Polarizable Continuum Model (PCM).

Starting 1-aryl-2-halogeno-3,3,3-trifluoropropenes 1a-l and 5a,b were synthesized and characterized previously.[2a-c]

General Procedure for Reaction of Styrenes 1a-l, 5a,b with Arenes in the Superacid CF_3SO_3H. Synthesis of Compounds 2a-zf, 4, 6a,b and 7a,b.

Stryrene **1** or **5** (0.3 mmol) was added dropwise to the stirred solution of arene (17 equiv. of benzene, or 5 equiv. of other arenes) in 1 mL of CF_3SO_3H. The mixture was stirred at temperature and time as indicated in Tables 3-5 (in case of reaction temperature -10 °C 0.5 mL of CH_2Cl_2 was added as co-solvent to increase the solubility of arene). Then reaction mixture was quenched with 100 mL of water. The aqueous layer was extracted with $CHCl_3$ (3×50 ml). The combined organic phases were washed with water (1×50 mL), saturated aqueous solution of $NaHCO_3$ (1×50 mL), and with water again (2×50 mL). The extract was dried over Na_2SO_4, and concentrated under reduced pressure. The crude mixture was purified by column chromatography with gradient elution with petroleum ether (40-70) to EtOAc. The yields and diastereomeric ratios for of compounds **2** are given in Table 2.

Synthesis of alkenes 3a-q.

General Procedure for Dehydrohalogenation of Compounds 2a-y in KOH-EtOH.

Compound **2** (0.1 mmol) was added to solution of KOH (1 mmol) in EtOH (2 mL). The reaction mixture was stirred at r. t. or with reflux for 15 or 20 h as indicated in Tables 3-5. Then it was diluted with 100 mL of Et_2O, washed with water (3×50 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The crude mixture was purified by column chromatography with gradient elution with petroleum ether (40-70) to EtOAc. The yields and Z-/E-ratios for compounds **3** are given in Table 2.

General procedure for dehydrohalogenation of compounds 2z-zf in t-BuOK-THF.

Tert-BuOK (1.1 mmol) was added to solution of compound **2** (0.1 mmol) in THF (1mL). The reaction mixture was stirred at r. t. (**2zb**) or with reflux (**2z, 2za, 2zc-2zf**) for 2 d. Then it was diluted with 100 mL of CH_2Cl_2, washed with water (3×50 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The crude mixture was purified by column chromatography with gradient elution with petroleum ether (40-70) to EtOAc. The yields and Z-/E-ratios for of compounds **3** are given in Table 2.

Compounds **3a-p** were obtained and characterized by ourselves previously,[18] except for **3c, 3f, 3q** (see their properties below).

*2-Chloro-1,1,1-trifluoro-3,3-diphenylpropane (**2a**).* Yield 73 mg, 86 %. Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 – 7.34 (m, 10H), 4.95 (dq, *J* = 8.2, 6.7 Hz, 1H), 4.52 (d, *J* 8.2 Hz, 1H). ^{13}C NMR (125

MHz, $CDCl_3$) δ 53.09, 59.70 (q, *J* = 29.9 Hz, $\underline{C}HCF_3$), 123.99 (q, *J* = 278.9 Hz, $\underline{C}F_3$), 127.38, 127.42, 127.88, 128.57, 128.67, 128.77, 139.46, 139.84. ^{19}F NMR (470 MHz, $CDCl_3$) δ -70.48 (d, *J* = 6.7 Hz); MS (GC-MS, EI), m/z, ($I_{rel.}$, %): 284 $[M]^+$ (7), 167 (100), 152 (25); HRMS (MALDI) m/z calcd for $C_{15}H_{13}ClF_3$ $[M+H]^+$ 285.0652, found 285.0654.

2-Chloro-1,1,1-trifluoro-3-(4-methylphenyl)-3-phenylpropane ***(2b)***. Obtained as a mixture of diastereomers **D1**(*1RS/2RS*) and **D2**(*1SR/2RS*). Yield 81 mg, 91 %. Colorless oil. **2b**-**D1***(1RS/2RS)*:^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 – 7.35 (m, 4H), 7.20 – 7.25 (m, 3H), 7.11 – 7.16 (m, 2H), 4.95 (dq, *J* = 8.7, 6.4 Hz, 1H, $C\underline{H}Cl$), 4.49 (d, *J* = 8.7 Hz, 1H, $C\underline{H}Ph$), 2.31 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.97 ($\underline{C}H_3$), 52.76 ($\underline{C}HPh$), 59.77 (q, *J* = 29.9 Hz, $\underline{C}Cl$), 124.01 (q, *J* = 278.4 Hz, $\underline{C}F_3$), D1+D2: 127.28, 127.33, 127.72, 127.82, 128.52, 128.54, 128.59, 128.75, 129.28, 129.45, 136.50, 136.86, 137.08, 137.12, 139.72, 140.09. ^{19}F NMR (470 MHz, $CDCl_3$) δ -70.42 (d, *J* = 6.4 Hz, $C\underline{F}_3$). **2b**-**D2***(1SR/2RS)*:^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 – 7.35 (m, 4H), 7.20 – 7.25 (m, 3H), 7.11 – 7.16 (m, 2H), 4.94 (dq, *J* = 8.7, 6.4 Hz, 1H, $C\underline{H}Cl$), 4.50 (d, *J* = 8.7 Hz, 1H, $C\underline{H}Ph$), 2.33 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (selected signals) 21.0 ($\underline{C}H_3$), 52.7 ($\underline{C}HPh$), 59.8 (q, $\underline{C}Cl$, *J* = 29.9 Hz), 124.0 (q, *J* = 278.4 Hz, $\underline{C}F_3$). ^{19}F NMR (470 MHz, $CDCl_3$) δ -70.47 (d, *J* = 6.4 Hz, $C\underline{F}_3$). MS (GC-MS, EI), m/z, ($I_{rel.}$, %) D1+D2: 298 $[M]^+$ (10), 181 (100), 165 (29), 89 (6). HRMS (MALDI) (D1+D2) m/z calcd for $C_{16}H_{15}ClF_3$ $[M+H]^+$ 299.0809, found 299.0811.

2-Chloro-1,1,1-trifluoro-3-(2,4-dimethylphenyl)-3-phenylpropane ***(2c)***. Obtained as a mixture of diastereomers **D1**(*1RS/2RS*) and **D2**(*1SR/2RS*). Yield 85 mg, 91 %. Colorless oil. **2c-D1** *(1RS/2RS)*:^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 – 7.35 (m, 5H), 7.08 – 7.11 (m, 3H), 4.92 – 4.98 (m, 1H, $C\underline{H}CF_3$), 4.46 (d, *J* = 8.8 Hz, 1H, $C\underline{H}Ph$), 2.24 (s, 3H), 2.22 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (selected signals) 19.30, 19.85, 52.82 (CHPh), 59.83 (q, *J* = 29.7 Hz, $\underline{C}HCF_3$), 124.04 (q, *J* = 278.8Hz, CF_3); ***D1+D2***: 125.1, 125.6, 127.2, 127.3, 127.8, 128.5, 128.6, 128.7, 129.1, 129.8, 129.9, 129.9, 135.7, 135.8, 136.8, 136.9, 137.0, 137.3, 139.8, 140.2. ^{19}F NMR (470 MHz, $CDCl_3$) δ -70.41 (d, J = 6.4 Hz). **2c-D2***(1SR/2RS)*:^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 – 7.35 (m, 5H), 7.08 – 7.11 (m, 3H), 4.92 – 4.98 (m, 1H, C<u>H</u>CF_3), 4.44 (d, 1H, J = 8.8 Hz, C<u>H</u>Ph), 2.26 (s, 3H), 2.24 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (selected signals) 19.3 (CH_3), 19.9 (CH_3), 53.0 (<u>C</u>HPh), 59.7 (q, J = 29.7 Hz, <u>C</u>HCF_3), 124.0 (q, J = 278.8Hz, CF_3). ^{19}F NMR (470 MHz, $CDCl_3$) δ -70.39 (d, J = 6.4 Hz). HRMS (MALDI) (D1+D2) m/z calcd for $C_{17}H_{17}ClF_3$ $[M+H]^+$ 313.0966, found 313.0968.

2-Chloro-1,1,1-trifluoro-3-(2,4-dimethylphenyl)-3-phenylpropane ***(2d)***.Obtained as a mixture of diastereomers **D1**(*1RS/2RS*) and **D2**(*1SR/2RS*). Yield 62 mg, 66 %. Colorless oil. **2d-D1***(1RS/2RS)*:^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 – 7.35 (m, 4H), 6.88 – 6.96 (m, 4H), 4.92 – 4.98 (m, 1H, C<u>H</u>CF_3), 4.45 (d, J = 9.5 Hz, 1H, C<u>H</u>Ph), 2.32 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (selected signals) 21.33, 52.94 (<u>C</u>HAr_2), 59.83 (q, J = 29.9 Hz, <u>C</u>HCF_3,), 124.05 (q, J = 278.8 Hz, CF_3), ***D1+D2***: 125.61, 126.2, 127.3, 127.3, 127.9, 128.5, 128.6, 128.7, 129.0, 129.1, 138.0, 138.1, 138.2, 139.5, 139.7, 139.7, 140.0. ^{19}F NMR (470 MHz, $CDCl_3$) δ -70.58 (d, J = 6.9 Hz). **2d-D2***(1SR/2RS)*:^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 – 7.35 (m, 4H), 6.88 – 6.96 (m, 4H), 4.92 – 4.98 (m, 1H, C<u>H</u>CF_3), 4.42 (d, J = 9.5 Hz, 1H, C<u>H</u>Ph), 2.32 s (3H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$) δ (selected signals) 21.4 (CH_3), 53.4 (<u>C</u>HAr_2), 59.7 (q, J = 29.9 Hz, <u>C</u>HCF_3), 124.0 (q, J = 278.8 Hz, CF_3). ^{19}F NMR (470 MHz, $CDCl_3$) δ -70.34 (d, J = 6.9 Hz). HRMS (MALDI) (D1+D2) m/z calcd for $C_{17}H_{17}ClF_3$ $[M+H]^+$ 313.0966, found 313.0960.

2-Chloro-1,1,1-trifluoro-3-(2,5-dimethylphenyl)-3-phenylpropane ***(2e)***. Obtained as a mixture of diastereomers **D1**(*1RS/2RS*) and **D2**(*1SR/2RS*). Yield 83 mg, 89 %. Colorless oil. **2e-D1***(1RS/2RS)*:^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 – 7.33 (m, 5H), 6.96 – 7.05 (m, 2H), 4.96 (dq, J =9.6, 5.8 Hz, 1H), 4.69 (d, J = 9.6 Hz, 1H), 2.40 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (selected signals) 19.4 (CH_3), 21.3 (CH_3), 49.01 (<u>C</u>HAr_2), 59.9 (q, J = 29.9 Hz, <u>C</u>HCF_3), 124.1 (q, J = 278.8 Hz, CF_3), ***D1+D2***: 126.7, 127.2, 127.2, 127.4, 127.8, 127.9, 128.4, 128.6, 128.1, 130.8, 130.9, 132.4, 133.29, 135.6, 135.7, 137.9, 138.3, 138.5, 139.1. ^{19}F NMR (470 MHz, $CDCl_3$) δ -69.92 (d, *J* = 5.8 Hz). **2e-D2***(1SR/2RS)*:^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 – 7.33 (m, 5H), 6.96 – 7.05 (m, 2H), 4.97 (dq, *J* = 9.6, 5.8 Hz, 1H, C<u>H</u>CF_3), 4.78 (d, *J* = 9.6 Hz, 1H, C<u>H</u>Ph), 2.40 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (selected signals) 19.4 (CH_3), 21.2 (CH_3), 47.7 (<u>C</u>HAr_2), 60.1 (q, *J* = 29.9 Hz, <u>C</u>HCF_3), 124.2 (q, *J* = 278.8 Hz, CF_3). ^{19}F NMR (470 MHz, $CDCl_3$) δ -70.95 (d, *J* = 5.8 Hz). HRMS (MALDI) (D1+D2) m/z calcd for $C_{17}H_{17}ClF_3$ $[M+H]^+$ 313.0966, found 313.0965.

*2-Chloro-1,1,1-trifluoro-3-(2,4,5-trimethylphenyl)-3-phenylpropane (**2f**).* Obtained in mixture with compounds **2g** in ratio **2f** : **2g** 5.2 : 1 in a whole yield 85 mg, 87 %. Mixture of diastereomers **D1**(*1RS/2RS*) and **D2**(*1SR/2RS*). Colorless oil. **2f-D1***(1RS/2RS)*:^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 – 7.31 (m, 6H), 6.93 (m, 1H), 4.96 (m, 1H, C<u>H</u>CF_3), 4.74 (d, *J* = 9.6 Hz, 1H, C<u>H</u>Ph), 2.31 (s, 3H), 2.29 (s, 3H), 2.21 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (selected signals) 19.17 (CH_3), 19.21 (CH_3), 19.70 (CH_3), 48.78 (<u>C</u>HAr_2), 60.10 (q, *J* = 29.7 Hz, <u>C</u>HCF_3,), 124.20 (q, *J* = 278.8 Hz, CF_3,), ***D1+D2***: 127.1, 127.3, 127.8, 128.4, 128.5, 128.6, 129.0, 129.9, 132.3, 132.4, 132.7, 133.6, 134.2, 134.3, 135.3, 135.4, 135.5, 135.8, 138.9, 139.4. ^{19}F NMR (470 MHz, $CDCl_3$) δ -69.93 (d, *J* = 6.4 Hz). **2f-D2***(1SR/2RS)*:^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 – 7.31 (m, 6H), 6.92 (m, 1H), 4.97 (m, 1H, C<u>H</u>CF_3), 4.65 (d, *J* = 9.6 Hz, 1H, C<u>H</u>Ph), 2.30 (s, 3H), 2.25 (s, 3H), 2.19 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (selected signals) 19.1 (CH_3), 19.2 (CH_3), 19.6 (CH_3), 47.5 (<u>C</u>HAr_2), 60.0 (q, *J* = 29.7 Hz, <u>C</u>HCF_3), 124.2 (q, *J* = 278.8 Hz, CF_3). ^{19}F NMR (470 MHz, $CDCl_3$) δ -70.90 (d, *J* = 6.4 Hz). MS (GC-MS, EI), m/z, ($I_{rel.}$, %) D1+D2: 326 $[M]^+$ (21), 209 (100), 194 (20), 179 (22), 165 (7). HRMS (MALDI) (D1+D2) m/z calcd for $C_{18}H_{19}ClF_3$ $[M+H]^+$ 327.1122, found 327.1119.

*2-Chloro-1,1,1-trifluoro-3-(2,3,5-trimethylphenyl)-3-phenylpropane (**2g**).* Obtained in mixture with compounds **2f** in ratio **2f** : **2g** 5.2 : 1 in a whole yield 85 mg, 87 %. Mixture of diastereomers **D1**(*1RS/2RS*) and **D2**(*1SR/2RS*). Colorless oil. **2g-D1***(1RS/2RS)*:^{1}H NMR (500 MHz, $CDCl_3$) δ 6.93 – 7.31 (m, 7H), 4.96 (m, 1H, C<u>H</u>CF$_3$), 4.87 (d, *J* = 9.8 Hz, 1H, C<u>H</u>Ph), 2.37 (s, 3H), 2.24 (s, 3H), 2.21 (s, 3H). ^{19}F NMR (470 MHz, CDCl$_3$) δ -69.75 (d, *J* = 6.4 Hz). **2f-D2***(1SR/2RS)*:^{1}H NMR (500 MHz, CDCl$_3$) δ 6.93 – 7.31 (m, 7H), 4.97 (m, 1H, C<u>H</u>CF$_3$), 4.76 (d, *J* = 9.8 Hz, 1H, C<u>H</u>Ph), 2.37 (s, 3H), 2.24 (s, 3H), 2.21 (s, 3H). ^{19}F NMR (470 MHz, CDCl$_3$) δ -70.94 (d, *J* = 6.4 Hz). HRMS (MALDI) (D1+D2) m/z calcd for $C_{18}H_{19}ClF_3$ [M+H]$^+$ 327.1122, found 327.1119

2-Chloro-1,1,1-trifluoro-3-(3,4-dichlorophenyl)-3-phenylpropane ***(2h)***. Obtained as a mixture of diastereomers **D1**(*1RS/2RS*) and **D2**(*1SR/2RS*). Yield 23 mg, 22 %. Colorless oil. **2h-D1***(1RS/2RS)*:^{1}H NMR (500 MHz, CDCl$_3$) δ 7.28 – 7.42 (m, 7H), 7.15 – 7.20 (m, 1H), 4.90 (dq, *J* = 8.4, 6.4 Hz, 1H, C<u>H</u>CF$_3$), 4.50 d (1H, *J* = 8.4 Hz, C<u>H</u>Ph). ^{19}F NMR (470 MHz, CDCl$_3$) δ -70.67 (d, *J* = 6.4 Hz). GC-MS: *m/z* ($I_{rel.}$, *%*) D1+D2: 352 [M]$^+$ (14), 235 (100), 200 (20), 179 (21), 165 (70). **2h-D2***(1SR/2RS)*:^{1}H NMR (500 MHz, CDCl$_3$) δ 7.28 – 7.42 (m, 7H), 7.15 – 7.20 (m, 1H), 4.89 (dq, *J* = 8.4, 6.4 Hz, 1H), 4.46 (d, *J* = 8.4 Hz, 1H), ^{19}F NMR (470 MHz, CDCl$_3$) δ -70.40 (d, *J* = 8.4 Hz). MS (GC-MS, EI), m/z, ($I_{rel.}$, %) D1+D2: 352 [M]$^+$ (14), 235 (100), 200 (20), 179 (21), 165 (70). HRMS (MALDI) (D1+D2) m/z calcd for $C_{15}H_{11}Cl_3F_3$ [M+H]$^+$ 352.9873, found 352.9872.

2-Chloro-1,1,1-trifluoro-3-(4-methoxyphenyl)-3-phenylpropane ***(2i)***. Obtained as a mixture of diastereomers **D1**(*1RS/2RS*) and **D2**(*1SR/2RS*). Yield 66 mg, 70 %. Colorless oil. **2i-*D1****(1RS/2RS)*:^{1}H NMR (500 MHz, CDCl$_3$) δ 7.22 – 7.34 (m, 7H), 6.84 (d, *J* = 8.7 Hz, 2H), 4.90 (dq, *J* =8.6, 6.0 Hz, 1H, C<u>H</u>CF$_3$), 4.47 (d, *J* = 8.6 Hz, 1H, C<u>H</u>Ph), 3.77 (s, 3H). ^{13}C NMR (125 MHz, CDCl$_3$) δ (selected signals) 52.4 (<u>C</u>HPh), 55.2 (OCH$_3$), 59.8 (q, *J* = 29.6 Hz, <u>C</u>ClCF$_3$), 114.1, 124.0 (q, *J* = 278.6 Hz, CF$_3$); ***D1+D2***:127.2, 127.3, 127.8, 128.5, 128.6, 128.7, 128.9, 129.8, 131,4, 131.9, 139.8, 140.2, 158.8. ^{19}F NMR (470 MHz, CDCl$_3$) δ -70.35 (d, *J* = 6.0 Hz). **2i-D2***(1SR/2RS)*:^{1}H NMR (500 MHz, CDCl$_3$) δ 7.22 – 7.34 (m, 7H), 6.87 (d, *J* = 8.7 Hz, 2H), 4.90 (dq, *J* =8.6, 6.0 Hz, 1H, C<u>H</u>CF$_3$), 4.49 (d, *J* = 8.6 Hz, 1H, C<u>H</u>Ph), 3.79 (s, 3H). ^{13}C NMR (125 MHz, CDCl$_3$) δ (selected signals) 51.9 (<u>C</u>HPh), 55.2 (OCH$_3$), 59.8

(q, *J* = 29.6 Hz, CClCF$_3$), 113.9, 124.0 (q, *J* = 278.6 Hz, CF$_3$). ^{19}F NMR (470 MHz, CDCl$_3$) δ -70.58 (d, *J* = 6.0 Hz). MS (GC-MS, EI), m/z, (I$_{rel.}$, %) D1+D2: 314 [M]$^+$ (11), 197 (100), 165 (14), 153(13). HRMS (MALDI) (D1+D2) m/z calcd for $C_{16}H_{15}ClF_3O$ [M+H]$^+$ 315.0758, found 315.0756.

2-Chloro-1,1,1-trifluoro-3-(3,4-dimethoxyphenyl)-3-phenylpropane ***(2j)***. Obtained as a mixture of diastereomers **D1**(*1RS/2RS*) and **D2**(*1SR/2RS*). Yield 44 mg, 43 %. Colorless oil. **2j**-**D1***(1RS/2RS)*:^{1}H NMR (500 MHz, CDCl$_3$) δ 7.31 – 7.34 (m, 4H), 6.78 – 6.89 (m, 3H), 4.91 (m, 1H, CHCF$_3$), 4.47 (d, *J* = 8.4 Hz, 1H, CHPh), 3.86 (s, 3H), 3.84 (s, 3H). ^{13}C NMR (125 MHz, CDCl$_3$) δ (selected signals) 52.6 (CHAr$_2$), 55.8 (OCH$_3$), 55.9 (OCH$_3$), 59.8 (q, CHCl, *J* = 29.9 Hz), 123.9 (q, CF$_3$, *J* = 278.8 Hz), ***D1+D2***: 111.1, 111.2, 111.4, 112.5, 120.1, 120.9, 127.3, 127.4, 127.8, 128.5, 129.7, 131.7, 132.3, 139.6, 140.0, 148.4, 148.8, 149.0. ^{19}F NMR (470 MHz, CDCl$_3$) δ -70.44 (d, *J* = 6.8 Hz). **2j-D2***(1SR/2RS)*:^{1}H NMR (500 MHz, CDCl$_3$) δ δ 7.31 – 7.34 (m, 4H), 6.78 – 6.89 (m, 3H), 4.92 (m, 1H, CHCF$_3$), 4.48 (d, *J* = 8.4 Hz, 1H, CHPh), 3.86 (s, 3H), 3.84 (s, 3H). ^{13}C NMR (125 MHz, CDCl$_3$) δ (selected signals) 52.3 (CHAr$_2$), 55.8 (OCH$_3$), 55.9 (OCH$_3$), 60.0 (q, *J* = 29.9 Hz, CHCl), 123.9 (q, CF$_3$, *J* = 278.8 Hz). ^{19}F NMR (470 MHz, CDCl$_3$) δ -70.49 (d, *J* = 6.8Hz). HRMS (MALDI) (D1+D2) m/z calcd for $C_{17}H_{17}ClF_3O_2$ [M+H]$^+$ 345.0864, found 345.0867.

2-Chloro-1,1,1-trifluoro-3-(3-methylphenyl)-3-phenylpropane ***(2k)***. Obtained as a mixture of diastereomers **D1**(*1RS/2RS*) and **D2**(*1SR/2RS*). Yield 70 mg, 78 %. Colorless oil. **2k-D1***(1RS/2RS)*:^{1}H NMR (500 MHz, CDCl$_3$) δ 7.06 – 7.37 (m, 9H), 4.98 (dq, *J* = 8.7, 6.5 Hz, 1H CHCF$_3$), 4.53 (d, *J* = 8.7 Hz, 1H, CHPh), 2.36 (s, 3H). ^{13}C NMR (125 MHz, CDCl$_3$) δ (selected signals) 21.0 (CH$_3$), 52.3 (CHPh), 59.7 (q, *J* = 29.9 Hz, CCl), 124.0 (q, *J* = 278.8 Hz, CF$_3$); **(D1+D2)**: 124.8, 125.4, 127.3, 127.4, 127.9, 128.1, 128.2, 128.4, 128.5, 129.6, 128.7, 129.4, 138.2, 138.4, 139.5, 139.6, 139.8, 139.9. ^{19}F NMR (470 MHz, CDCl$_3$) δ -69.95 (d, *J* = 6.5 Hz). MS: *m/z (I$_{rel.}$, %)*: 300 [M+2]$^+$ (4), 298 [M]$^+$ (12), 181 (100), 165 (31), 89(7). **2k-D2***(1SR/2RS)*:^{1}H NMR (500 MHz, CDCl$_3$) δ 7.06 – 7.37 (m, 9H), 4.97 (dq, *J* = 8.7, 6.5

Hz, 1H C<u>H</u>CF_3), 4.49 (d, *J* = 8.7 Hz, 1H, C<u>H</u>Ph), 2.34 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (selected signals) 20.9 (CH_3), 52.8 (<u>C</u>HPh), 59.7 (q, *J* = 29.9 Hz, <u>C</u>Cl), 124.0 (q, *J* = 278.8 Hz, <u>C</u>F_3). ^{19}F NMR (470 MHz, $CDCl_3$) δ -70.07 (d, *J* = 6.5 Hz). MS (GC-MS, EI), m/z, ($I_{rel.}$, %) D1+D2: 298 $[M]^+$ (12), 181 (100), 165 (31), 89(7). HRMS (MALDI) (D1+D2) m/z calcd for $C_{16}H_{15}ClF_3$ $[M+H]^+$ 299.0809, found 299.0810.

*2-Chloro-1,1,1-trifluoro-3-(4-methoxyphenyl)-3-(4-methylphenyl)propane (**2l**)*. Obtained as a mixture of diastereomers **D1**(*1RS/2RS*) and **D2**(*1SR/2RS*). Yield 65 mg, 66 %. Colorless oil. **2l-D1***(1RS/2RS)*:^{1}H NMR (500 MHz, $CDCl_3$) δ 7.11 – 7.24 (m, 6H), 6.86 (d, *J* = 8.7 Hz, 2H), 4.91 (m, 1H, C<u>H</u>CF_3), 4.46 (d, *J* = 8.3 Hz, 1H, C<u>H</u>Ar), 3.79 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (selected signals) 20.1 (CH_3), 51.6, 55.2, 60.1 (q, *J* = 29.7 Hz, <u>C</u>Cl), ***D1+D2***: 113.9, 114.1, 124.0 (q, *J* = 278.8 Hz, CF_3), 127.6, 128.3, 128.9, 129.3, 129.4, 128.8, 131.7, 132.2, 136.8, 136.9, 137.0, 137.2, 158.7. ^{19}F NMR (470 MHz, $CDCl_3$) δ -70.52 (d, *J* = 6.3 Hz). GS-MS: *m/z ($I_{rel.}$, %)*: 328.2 $[M]^+$ (11), 211.3 (100), 165.2 (9). **2l-D2***(1SR/2RS)*:^{1}H NMR (500 MHz, $CDCl_3$) δ 7.11 – 7.24 (m, 6H), 6.83 (d, *J* = 8.7 Hz, 2H), 4.89 (m, 1H, C<u>H</u>CF_3), 4.44 (d, *J* = 8.3 Hz, 1H, C<u>H</u>Ar), 3.77 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (selected signals) 21.0 (<u>C</u>H_3), 51.9, 55.2 (O<u>C</u>H_3), 59.9 (q, *J* = 29.7 Hz, <u>C</u>Cl). ^{19}F NMR (470 MHz, $CDCl_3$) δ -70.34 (d, *J* = 6.3 Hz). HRMS (MALDI) (D1+D2) m/z calcd for $C_{17}H_{17}ClF_3O$ $[M+H]^+$ 329.0915, found 329.0912.

*2-Chloro-1-(4-chlorophenyl)-3,3,3-trifluoro-1-phenylpropane (**2m**)*. Obtained as a mixture of diastereomers **D1**(*1RS/2RS*) and **D2**(*1SR/2RS*). Yield 87 mg, 91 %. Colorless oil. **2m-D1***(1RS/2RS)*:^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 – 7.35 (m, 9H), 4.91 (dq, *J* = 8.4, 6.8 Hz, 1H, C<u>H</u>CF_3), 4.52 (d, *J* = 8.4 Hz, 1H, C<u>H</u>Ph). ^{13}C NMR (125 MHz, $CDCl_3$) δ (selected signals) 52.1 (<u>C</u>HPh), 59.4 (q, *J* = 30.2 Hz, <u>C</u>Cl), 123.9 (q, *J* = 278.7 Hz, CF_3). ***D1+D2***: 127.6, 127.7, 128.5, 128.7, 128.9, 129.0, 129.2, 130.1, 133.4, 137.8, 138.3, 138.9, 139.3. ^{19}F NMR (470 MHz, $CDCl_3$) δ -70.61 (d, *J* = 6.8 Hz). GS-MS: *m/z ($I_{rel.}$, %)*: 318 $[M]^+$ (11), 201 (100), 165 (45), 83 (5). **2m-D2***(1SR/2RS)*:^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 – 7.35

(m, 9H), 4.91 (dq, *J* = 8.4, 6.8 Hz, 1H, C<u>H</u>CF_3), 4.50 (d, *J* = 8.4 Hz, 1H, C<u>H</u>Ph,). ^{13}C NMR (125 MHz, $CDCl_3$) δ (selected signals) 52.5 (<u>C</u>HPh), 59.4 (q, *J* = 30.2 Hz, <u>C</u>Cl), 123.9 (q, *J* = 278.7 Hz, CF_3). ^{19}F NMR (470 MHz, $CDCl_3$) δ -70.38 (d, *J* = 6.8 Hz). HRMS (MALDI) (D1+D2) m/z calcd for $C_{15}H_{12}Cl_2F_3$ $[M+H]^+$ 319.0263, found 319.0260.

*2-Chloro- 1-(4-chlorophenyl)-3,3,3-trifluoro-1-(4-methoxyphenyl)propane (**2n**)*. Obtained as a mixture of diastereomers **D1**(*1RS/2RS*) and **D2**(*1SR/2RS*). Yield 85 mg, 81 %. Colorless oil. **2n-D1***(1RS/2RS)*:^{1}H NMR (500 MHz, $CDCl_3$) δ 7.18 – 7.31 (m, 6H),6,84 (d, *J* = 8.7 Hz, 2H), 4.85 (m, 1H, C<u>H</u>CF_3), 4.48 (d, *J* = 8.1 Hz, 1H), 3.78 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (selected signals) 51.4 (<u>C</u>HAr), 55.2 (O<u>C</u>H_3), 59.6 (q, *J* = 30.1 Hz, <u>C</u>Cl), ***D1+D2***: 114.0, 114.2, 123.7 (q, *J* = 278.4 Hz, CF_3), 128.7, 128.8, 128.9, 129.1, 129.8, 130.0, 130.8, 131.4, 133.2, 138.1, 138.7, 158.8, 158.9 (C_{arom}). ^{19}F NMR (470 MHz, $CDCl_3$) δ -70.48 (d, *J* = 7.6 Hz). GS-MS: *m/z* ($I_{rel.}$, *%*): 348 $[M]^+$ (9.5), 231 (100), 196 (8), 153(14). **2n-D2***(1SR/2RS)*:^{1}H NMR (500 MHz, $CDCl_3$) δ 7.18 – 7.31 (m, 6H),6,87 (d, *J* = 8.7 Hz, 2H), 4.86 (m, 1H, C<u>H</u>CF_3), 4.47 (d, *J* = 8.1 Hz, 1H), 3.79 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) (selected signals) δ 51.35 (<u>C</u>HAr), 55.20 (O<u>C</u>H_3), 59.75 (q, *J* = 30.1 Hz, <u>C</u>Cl). ^{19}F NMR (470 MHz, $CDCl_3$) δ-70.47 (d, *J* = 7.6 Hz). HRMS (MALDI) (D1+D2) m/z calcd for $C_{16}H_{14}Cl_2F_3O$ $[M+H]^+$ 349.0368, found 349.0371.

*2-Chloro-1-(4-chlorophenyl)-1-(3,4-dichlorophenyl)-3,3,3-trifluoropropane (**2o**).*Obtained as a mixture of diastereomers **D1**(*1RS/2RS*) and **D2**(*1SR/2RS*). Yield 106 mg, 91 %. Colorless oil. **2o-D1***(1RS/2RS)*:^{1}H NMR (500 MHz, $CDCl_3$) δ 7.14 – 7.43 (m, 7H), 4.83 (m, 1H, C<u>H</u>CF_3), 4.47 (d, *J* = 7.5 Hz, 1H, C<u>H</u>Ar). ^{13}C NMR (125 MHz, $CDCl_3$) δ (selected signals) 51.3 (<u>C</u>HAr), 59.0 (q, *J* = 31.0 Hz, <u>C</u>Cl), 123.6 (q, *J* = 279.0 Hz, CF_3). ***D1+D2***: 127.1, 127.7, 128.0, 128.6, 129.0, 129.1, 129.2, 130.1, 130.5, 130.6, 130.8, 130.8, 131.2, 132.0, 132.8, 133.9, 136.5, 137.2, 138.9, 139.4 (C_{arom}). ^{19}F NMR (470 MHz, $CDCl_3$) δ -66.20 (d, *J* = 7.5 Hz). GS-MS: *m/z* ($I_{rel.}$, *%*):386 $[M]^+$ (13), 269 (100), 233 (15), 199 (59), 163 (10). **2o-D2***(1SR/2RS)*:^{1}H NMR (500 MHz, $CDCl_3$) δ 7.14 – 7.43 (m, 7H), 4.83 (m, 1H, C<u>H</u>CF_3), 4.47 (d, *J* = 7.5

Hz, 1H, CHAr). ^{13}C NMR (125 MHz, $CDCl_3$) δ (selected signals) 51.1 (CHAr), 59.0 (q, *J* = 31.0 Hz, CCl), 123.6 (q, *J* = 279.0 Hz, CF_3). ^{19}F NMR (470 MHz, $CDCl_3$) δ -66.22 (d, *J* = 7.5 Hz). HRMS (MALDI) (D1+D2) m/z calcd for $C_{15}H_{10}Cl_4F_3$ $[M+H]^+$ 386.9483, found 386.9484.

2-Chloro-1,1,1-trifluoro-3,3-bis(4-methoxyphenyl)propane ***(2p)***. Yield 92 mg, 89 %.Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (d, J = 8.6 Hz, 2H), 7.21 (d, J = 8.3 Hz, 2H), 6.86 (d, J = 8.6 Hz), 6.83 (f, J = 8.3 Hz), 4.86 (dq, *J* = 8.4, 5.9 Hz, 1H, $CHCF_3$), 4.45 (d, *J* = 8.4 Hz, 1H, CHPh), 3.79 (s, 3H), 3.77 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 51.2 ($CHAr_2$), 55.1 (OCH_3), 55.2 (OCH_3), 60.2 (q, *J* = 29.7 Hz, $CHCF_3$), 113.9, 114.1, 124.9 (q, *J* = 278.8 Hz, CF_3), 128.8, 129.7, 131.8, 132.3, 158.7. ^{19}F NMR (470 MHz, $CDCl_3$) δ -70.44 (d, *J* = 5.9 Hz). GS-MS: *m/z* ($I_{rel.}$, *%*): 344 $[M]^+$ (7), 227 (100), 212(6), 169(6), 113(10). HRMS (MALDI) m/z calcd for $C_{17}H_{17}ClF_3O_2$ $[M+H]^+$ 345.0864, found 345.0865.

2-Chloro-1,1,1-trifluoro-3-(4-methoxyphenyl)-3-(3,4-dimethoxyphenyl)propane ***(2q)***.Obtained as a mixture of diastereomers **D1**(*1RS/2RS*) and **D2**(*1SR/2RS*). Yield 30 mg, 27 %. Colorless oil. **2q-D1***(1RS/2RS)*:^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21 – 7.25 (m, 2H), 6.77 – 6.90 (m, 5H), 4.85 (m, 1H, $CHCF_3$), 4.45 (d, *J* = 8.4 Hz, 1H, $CHAr_2$), 3.86 (s, 3H), 3.84 (s, 3H), 3.79 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (selected signals) 51.6 ($CHAr_2$), 55.2, 55.8, 55.9, 60.1 (q, *J* = 29.7 Hz, CCl), ***D1+D2***: 111.0, 111.2, 111.3, 112.3, 113.9, 114.1, 119.9, 120.6, 124.0 (q, *J* = 278.8 Hz, CF_3), 125.7, 128.8, 129.7, 131.5, 132.0, 132.1, 132.7, 148.2, 148.8, 149.0, 158.7. ^{19}F NMR (470 MHz, $CDCl_3$) δ -70.55 (d, *J* = 6.4 Hz). **2q-D2***(1SR/2RS)*:^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21 – 7.25 (m, 2H), 6.77 – 6.90 (m, 5H), 4.85 (m, 1H, $CHCF_3$), 4.43 (d, *J* = 8.4 Hz, 1H, $CHAr_2$), 3.86 (s, 3H), 3.83 (s, 3H), 3.77 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (selected signals) 51.4 ($CHAr_2$), 55.2, 55.8, 55.9, 60.1 (q, *J* = 29.7 Hz, CCl). ^{19}F NMR (470 MHz, $CDCl_3$) δ -70.38 (d, *J* = 6.4 Hz). HRMS (MALDI) m/z calcd for $C_{18}H_{19}ClF_3O_3$ $[M+H]^+$ 375.0969 found 375.0973.

*2-Bromo-1,1,1-trifluoro-3,3-diphenylpropane (**2r**)*. Yield 87 mg, 88 %. Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 – 7.35 (m, 10H), 4.98 (dq, *J* = 9.0, 6.6 Hz, 1H, C<u>H</u>CF_3), 4.54 (d, *J* = 9.0 Hz, 1H, C<u>H</u>Ph). ^{13}C NMR (125 MHz, $CDCl_3$) δ 50.0 (q, *J* = 29.0 Hz, <u>C</u>HCF_3), 53.6 (<u>C</u>HPh_2), 123.9 (q, *J* = 277.0 Hz, CF_3), 127.3, 127.4, 127.8, 128.3, 128.6, 128.7, 128.8, 140.1, 140.6. ^{19}F NMR (470 MHz, $CDCl_3$) δ -63.27 (d, *J* = 6.6 Hz). MS (GC-MS, EI), m/z, ($I_{rel.}$, %) D1+D2: 330 $[M+2]^+$ (10), 328 $[M]^+$ (10), 167 (100), 152 (15). HRMS (MALDI) m/z calcd for $C_{15}H_{13}BrF_3$ $[M+H]^+$ 329.0147, found 329.0149.

*2-Bromo-1,1,1-trifluoro-3-(2,5-dimethylphenyl)-3-phenylpropane (**2s**)*. Yield 72 mg, 67 %. Obtained as a mixture of diastereomers **D1**(*1RS/2RS*) and **D2**(*1SR/2RS*). Colorless oil. **2s-D1***(1RS/2RS)*:^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.31 (m, 6H), 6.92 –7.02 (m, 2H), 4.98 (m, 1H, C<u>H</u>CF_3), 4.71 (d, *J* = 9.2 Hz, 1H, C<u>H</u>Ph), 2.38 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (selected signals) 19.3, 21.3, 49.5 (<u>C</u>HPh), 50.3 (q, *J* = 29.2 Hz, <u>C</u>Br), 124.1 (q, *J* = 277.5 Hz, CF_3). ***D1+D2***: 126.4, 127.1, 127.2, 127.4, 127.8, 127.9, 128.4, 128.5, 128.6, 128.7, 130.8, 130.9, 132.3, 133.0, 135.6, 138.5, 138.9, 139.0, 140.1. ^{19}F NMR (470 MHz, $CDCl_3$) δ -67.03 (d, *J* = 7.0 Hz). **2s-D2***(1SR/2RS)*:^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.31 (m, 6H), 6.92 –7.02 (m, 2H), 4.97 (m, 1H, C<u>H</u>CF_3), 4.77 (d, *J* = 9.2 Hz, 1H, C<u>H</u>Ph), 2.33 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (selected signals) 19.4, 21.2, 50.0 (<u>C</u>HPh), 50.7 (q, *J* = 29.2 Hz, <u>C</u>Br), 124.1 (q, *J* = 277.5 Hz, CF_3). ^{19}F NMR (470 MHz, $CDCl_3$) δ -68.08 (d, *J* = 7.0 Hz). HRMS (MALDI) (D1+D2) m/z calcd for $C_{17}H_{17}BrF_3$ $[M+H]^+$ 357.0460, found 357.0462.

*2-Bromo-1,1,1-trifluoro-3-(4-methoxyphenyl)-3-phenylpropane (**2t**)*. Obtained as a mixture of diastereomers **D1**(*1RS/2RS*) and **D2**(*1SR/2RS*). Yield 102 mg, 95 %. Colorless oil. **2t-D1***(1RS/2RS)*:^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 – 7.34 (m, 7H), 6.82 (d, *J* = 8.7 Hz, 2H), 4.91 (dq, *J* = 8.9, 7.0 Hz, 1H, C<u>H</u>CF_3), 4.48 (d, *J* = 8.9 Hz, 1H, C<u>H</u>Ph), 3.76 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (selected signals) 50.3 (q, *J* = 29.0 Hz, <u>C</u>HCF_3), 52.9 (<u>C</u>HAr_2), 55.2 (OCH_3), 123.9 (q, *J* = 277.0 Hz, CF_3) ***D1+D2***: 113.9, 114.1, 127.2, 127.3, 127.7, 128.2, 128.5, 128.6, 128.7, 128.9, 129.6, 132.2, 132.6, 140.5, 140.9, 158.7, 158.8. ^{19}F NMR (470 MHz, $CDCl_3$) δ -67.47 (d, *J* = 7.0 Hz). **2t-D2***(1SR/2RS)*:^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 – 7.34 (m, 7H), 6.83 (d, *J* = 8.7 Hz, 2H), 4.90 (dq, *J* = 8.9, 7.0 Hz, 1H, $CHCF_3$), 4.51 (d, *J* = 8.9 Hz, 1H, CHPh), 3.78 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (selected signals) 50.6 (q, *J* = 29.0 Hz, $CHCF_3$), 52.4 ($CHAr_2$), 55.2 (OCH_3), 123.9 (q, *J* = 277.0 Hz, CF_3). ^{19}F NMR (470 MHz, $CDCl_3$) δ -67.72 (d, *J* = 7.0 Hz). MS (GC-MS, EI), m/z, ($I_{rel.}$, %) D1+D2: 360 $[M+2]^+$ (10), 358 $[M]^+$ (10), 197 (100), 165 (15), 153(12). HRMS (MALDI) (D1+D2) m/z calcd for $C_{16}H_{15}BrF_3O$ $[M+H]^+$ 359.0253, found 359.0255.

*2-Bromo-1,1,1-trifluoro-3-(3,4-dimethoxyphenyl)-3-phenylpropane (**2u**).* Yield 93 mg, 80 %. Obtained as a mixture of diastereomers **D1**(*1RS/2RS*) and **D2**(*1SR/2RS*). Yelowish oil. **2u-D1***(1RS/2RS)*:^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 – 7.35 (m, 5H), 6.77 – 6.89 (m, 3H), 4.92 (m, 1H, $CHCF_3$), 4.48 (d, *J* = 9.0 Hz, 1H, CHPh), 3.86 (s, 3H), 3.87 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (selected signals) 50.2 (q, *J* = 28.6 Hz, CBr), 53.1 (CHPh), 55.8, 55.9, 123.9 (q, *J* = 277.5 Hz, CF_3). ***D1+D2***: 111.0, 111.2, 111.3, 112.2, 120.0, 120.6, 127.2, 127.3, 127.4, 127.7, 128.2, 128.5, 128.7, 132.6, 132.9, 140.3, 140.7, 148.4, 148.8, 149.0. ^{19}F NMR (470 MHz, $CDCl_3$) δ -67.56 (d, *J* = 6.4 Hz). **2u-D2***(1SR/2RS)*:^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 – 7.35 (m, 5H), 6.77 – 6.89 (m, 3H), 4.92 (m, 1H, $CHCF_3$), 4.48 (d, *J* = 9.0 Hz, 1H, CHPh), 3.85 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (selected signals) 50.6 (q, *J* = 28.6 Hz, CBr), 52.7 (CHPh), 55.8, 56.0, 123.9 (q, *J* = 277.5 Hz, CF_3). ^{19}F NMR (470 MHz, $CDCl_3$) δ -67.65 (d, *J* = 6.4 Hz). HRMS (MALDI) (D1+D2) m/z calcd for $C_{17}H_{17}BrF_3O_2$ $[M+H]^+$ 389.0359, found 389.0371.

*2-Bromo-1-(4-chlorophenyl)-3,3,3-trifluoro-1-phenylpropane (**2v**).* Obtained as a mixture of diastereomers **D1**(*1RS/2RS*) and **D2**(*1SR/2RS*). Yield 83 mg, 73 %. Colorless oil. **2v-D1***(1RS/2RS)*:^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 – 7.35 (m, 9H), 4.91 (m, 1H, $CHCF_3$), 4.54 (d, *J* = 9.0 Hz, 1H, CHPh). ^{13}C NMR (125 MHz, $CDCl_3$) δ (selected signals) 49.8 (q, *J* = 29.4 Hz, $CBrCF_3$), 52.6 (CHPh), 123.8 (q, *J* = 277.5 Hz, CF_3) ***D1+D2***: 127.6, 127.7, 128.1, 128.2, 128.7, 128.9, 129.0, 129.1, 129.9, 130.5, 133.3, 133.4, 138.6, 138.9, 139.7, 140.1. ^{19}F NMR (470 MHz, $CDCl_3$) δ -67.76 (d, *J* = 6.8 Hz). **2v-**

D2_(1SR/2RS)_:[1]H NMR (500 MHz, $CDCl_3$) δ 7.23 – 7.35 (m, 9H), 4.91 (m, 1H, C<u>H</u>CF_3), 4.50 (d, *J* = 9.0 Hz, 1H, C<u>H</u>Ph). [13]C NMR (125 MHz, $CDCl_3$) δ (selected signals) 49.8 (q, *J* = 29.4 Hz, <u>C</u>Br), 53.0 (<u>C</u>HPh), 123.8 (q, *J* = 277.5 Hz, CF_3). [19]F NMR (470 MHz, $CDCl_3$) δ -67.51 (d, *J* = 6.8 Hz). MS (GC-MS, EI), m/z, ($I_{rel.}$, %) D1+D2: 362 $[M]^+$ (8), 201 (100), 178 (10), 165 (36). HRMS (MALDI) (D1+D2) m/z calcd for $C_{15}H_{12}BrClF_3$ $[M+H]^+$ 362.9758, found 362.9760.

2-Bromo-1-(4-chlorophenyl)-3,3,3-trifluoro-1-(methoxyphenyl)propane ***(2w)***. Obtained as a mixture of diastereomers **D1**(*1RS/2RS*) and **D2**(*1SR/2RS*). Yield 61 mg, 52 %. Yellowish oil. **2w-D1**_(1RS/2RS)_:[1]H NMR (500 MHz, $CDCl_3$) δ 7.17 – 7.31 (m, 6H), 6.87 (d, *J* = 8.7 Hz, 2H), 4.86 (m, 1H, C<u>H</u>CF_3), 4.47 (d, *J* = 8.2 Hz, 1H, C<u>H</u>Ar), 3.79 (s, 3H). [13]C NMR (125 MHz, $CDCl_3$) δ (selected signals) 50.2 (q, *J* = 29.4 Hz, <u>C</u>HCF_3), 51.8 (<u>C</u>HAr_2), 55.2, ***D1+D2***: 114.0, 114.2, 123.8 (q, *J* = 277.5 Hz, <u>C</u>F_3), 128.7, 128.8, 128.9, 129.0, 129.4, 129.7, 131.7, 132.0, 133.1, 133.2, 139.0, 139.2, 158.9. [19]F NMR (470 MHz, $CDCl_3$) δ -67.55 (d, *J* = 6.3 Hz). MS (GC-MS, EI), m/z, ($I_{rel.}$, %) D1+D2: 394 $[M+2]^+$ (8), 392 $[M]^+$ (6), 231 (100), 196 (7), 153(10). **2w-D2**_(1SR/2RS)_:[1]H NMR (500 MHz, $CDCl_3$) δ 7.17 – 7.31 (m, 6H), 6.83 (d, *J* = 8.7 Hz, 2H), 4.87 (m, 1H, C<u>H</u>CF_3), 4.49 (d, *J* = 8.2 Hz, 1H, C<u>H</u>Ar), 3.77 (s, 3H). [13]C NMR (125 MHz, $CDCl_3$) δ (selected signals) 50.0 (q, *J* = 29.4 Hz, <u>C</u>HCF_3), 51.9 (<u>C</u>HAr_2), 55.2 (OCH_3). [19]F NMR (470 MHz, $CDCl_3$) δ -67.55 (d, *J* = 6.3 Hz). HRMS (MALDI) (D1+D2) m/z calcd for $C_{16}H_{14}ClBrF_3O$ $[M+H]^+$ 392.9863, found 392.9855.

2-Bromo-1,1,1-trifluoro-3,3-bis(4-methoxyphenyl)propane ***(2x)***. Yield 106 mg, 91 %. Yellowish oil. [1]H NMR (500 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8.7 Hz, 2H), 7.20 (d, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 8.7 Hz, 2H), 6.82 (d, *J* = 8.6 Hz, 2H), 4.88 (dq, *J* = 9.0, 6.6 Hz, 1H, C<u>H</u>CF_3), 4.46 (d, *J* = 9.0 Hz, 1H, C<u>H</u>Ph), 3.78 (s, 3H), 3.76 (s, 3H). [13]C NMR (125 MHz, $CDCl_3$) δ 50.8 (q, *J* = 29.0 Hz, <u>C</u>HCF_3), 51.7 (<u>C</u>HAr_2), 55.0 (2O<u>C</u>H_3), 113.9, 114.1, 123.9 (q, *J* = 277.0 Hz, CF_3), 128.8, 129.4, 132.6, 132.9, 158.7. [19]F NMR (470

MHz, $CDCl_3$) δ -63.22 (d, *J* = 6.6 Hz). MS (GC-MS, EI), m/z, ($I_{rel.}$, %): 390 $[M+2]^+$ (10), 388 $[M]^+$ (10), 227 (100). HRMS (MALDI) m/z calcd for $C_{17}H_{17}BrF_3O_2$ $[M+H]^+$ 389.0359, found 389.0358.

2-Bromo-1,1,1-trifluoro-3-(4-methoxyphenyl)-3-(3,4-dimethoxyphenyl)propane ***(2y)****.* Obtained as a mixture of diastereomers **D1**(*1RS/2RS*) and **D2**(*1SR/2RS*). Yield 58 mg, 46 %. Colorless oil. **2y-D1***(1RS/2RS)*: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20 – 7.24 (m, 2H), 6.75 – 6.87 (m, 5H), 4.87 (m, 1H, C<u>H</u>CF_3), 4.45 (d, *J* = 7.8 Hz, 1H, C<u>H</u>Ar_2), 3.86 (s, 3H), 3.83 (s, 3H), 3.79 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (selected signals) 50.7 (q, *J* = 29.0 Hz, <u>C</u>HCF_3), 51.8 (<u>C</u>HAr_2), 55.2 (O<u>C</u>H_3), 55.8 (O<u>C</u>H_3), 55.9 (O<u>C</u>H_3), ***D1+D2***: 111.0, 111.2, 111.3, 112.1, 112.3, 113.8, 114.1, 119.8, 120.3, 123.9 (q, *J* = 276.6 Hz, CF_3), 128.7, 128.8, 129.4, 132.3, 132.6, 133.0, 133.2, 148.2, 148.8, 149.0, 158.7. ^{19}F NMR (470 MHz, $CDCl_3$) δ -67.65 (d, *J* = 7.0 Hz). **2y-D2***(1SR/2RS)*: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20 – 7.24 (m, 2H), 6.75 – 6.87 (m, 5H), 4.87 (m, 1H, C<u>H</u>CF_3), 4.43 (d, *J* = 7.8 Hz, 1H, C<u>H</u>Ar_2), 3.86 (s, 3H), 3.84 (s, 3H), 3.77 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (selected signals) 50.7 (q, *J* = 29.0 Hz, <u>C</u>HCF_3), 52.0 (<u>C</u>HAr_2), 55.2 (O<u>C</u>H_3), 55.8 (O<u>C</u>H_3), 55.9 (O<u>C</u>H_3) ^{19}F NMR (470 MHz, $CDCl_3$) δ -67.49 (d, *J* = 7.0 Hz). HRMS (MALDI) (D1+D2) m/z calcd for $C_{18}H_{19}BrF_3O_3$ $[M+H]^+$ 419.0464, found 419.0467.

1,1,1,2-Tetrafluoro-3,3-diphenylpropane ***(2z)****.* Yield 63 mg, 78 %. Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 – 7.34 (m, 10H), 4.95 (ddq, $J_{H–F}$ = 45.3 Hz, *J* = 6.7, 6.3 Hz, 1H, C<u>H</u>F), 4.43 (dd, $J_{H–F}$ = 21.6 Hz, *J* = 6.7 Hz, 1H, C<u>H</u>Ph). ^{19}F NMR (470 MHz, $CDCl_3$) δ -70.48 (dd, *J* = 11.5, 6.3 Hz, C<u>F</u>$_3$), -200.37 (ddq, J = 45.7, 21.6, 11.5 Hz, C<u>F</u>). HRMS (MALDI) m/z calcd for $C_{15}H_{13}F_4$ $[M+H]^+$ 269.0948, found 269.0950.

1,1,1,2-Tetrafluoro-3-(4-methylphenyl)-3-phenylpropane ***(2za)****.* Obtained as a mixture of diastereomers **D1**(*1RS/2RS*) and **D2**(*1SR/2RS*). Yield 57 mg, 67 %. Colorless oil. **2za-D1***(1RS/2RS)*: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.12 – 7.32 (m, 9H), 5.37 (ddq, $J_{H–F}$ = 45.4 Hz, *J* = 6.7, 6.1 Hz, 1H, C<u>H</u>F), 4.38 (dd, $J_{H–F}$ = 21.4 Hz, *J* = 6.7 Hz, 1H, C<u>H</u>Ph), 2.31 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (selected signals) 29.7

(CH_3), 50.2 (d, *J* = 19.6 Hz, <u>C</u>HPh), 89.8 (dq, *J* = 190.0, 31.7 Hz, <u>C</u>F), **(D1+D2)**: 124.0 (qd, *J* = 281.0, 26.3Hz, <u>C</u>F_3), 127.29, 127.4, 128.0, 128.1, 128.6, 128.7, 128.8, 128.9, 129.3, 129.6, 134.9, 135.8, 135.9, 137.06, 137.2, 138.2. ^{19}F NMR (470 MHz, $CDCl_3$) δ -76.32 (dd, *J* = 11.7, 6.1 Hz), -200.09 (ddq, *J* = 45.4, 21.4, 11.7 Hz, F). **2za-D2***(1SR/2RS)*:^{1}H NMR (500 MHz, $CDCl_3$) δ 7.12 – 7.32 (m, 9H), 5.37 (ddq, $J_{H–F}$ = 45.4 Hz, *J* = 6.7, 6.1 Hz, 1H, C<u>H</u>F), 4.38 (dd, $J_{H–F}$ = 21.4, *J* = 6.7 Hz, 1H, C<u>H</u>Ph), 2.32 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (selected signals) 29.7 (CH_3), 50.2 (d, *J* = 19.6 Hz, <u>C</u>HPh), 89.8 (dq, *J* = 190.0, 31.7 Hz, <u>C</u>F). ^{19}F NMR (470 MHz, $CDCl_3$) δ -76.34 (dd, *J* = 11.7, 6.1 Hz), -200.44 (ddq, J = 45.4, 21.4, 11.7 Hz, F). HRMS (MALDI) (D1+D2) m/z calcd for $C_{16}H_{15}F_4$ $[M+H]^+$ 283.1104, found 283.1105.

*1-(4-Chlorophenyl)-2,3,3,3-tetrafluoro-1-phenylpropane (**2zb**).* Obtained as a mixture of diastereomers **D1***(1RS/2RS)* and **D2***(1SR/2RS)*. Yield 83 mg, 92 %. Colorless oil. **2zb-D1***(1RS/2RS)*:^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 – 7.36 (m, 9H), 4.99 (d quintets, $J_{H–F}$ = 45.2 Hz, *J* = 6.1 Hz, 1H, C<u>H</u>F), 4.42 (dd, $J_{H–F}$ = 22.4 Hz, *J* = 6.1 Hz, 1H, C<u>H</u>Ph). ^{13}C NMR (125 MHz, $CDCl_3$) δ (selected signals) 49.8 (d, *J* = 19.2 Hz, <u>C</u>HPh), 89.4 (dq, *J* = 190.9, 32.1 Hz, <u>C</u>F), 122.5 (qd, *J* = 280.8, 26.8 Hz, <u>C</u>F_3), **(D1+D2)**: 127.6, 127.7, 128.0, 128.7, 128.8, 128.9, 129.0, 129.1, 129.4, 130.3, 133.4, 133.5, 136.2, 137.3, 138.4, 138.5. ^{19}F NMR (470 MHz, $CDCl_3$) δ -76.21 (dd, *J* = 11.4, 6.1 Hz), -137.34 (ddq, J = 45.2, 22.4, 11.4 Hz, F). **2zb-D2***(1SR/2RS)*:^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 – 7.36 (m, 9H), 4.99 (d quintets, $J_{H–F}$ = 45.2 Hz, *J* = 6.1 Hz, 1H, C<u>H</u>F), 4.42 (dd, $J_{H–F}$ = 22.4 Hz, *J* = 6.1 Hz, 1H, C<u>H</u>Ph). ^{13}C NMR (125 MHz, $CDCl_3$) δ (selected signals) 49.7 (d, *J* = 19.2 Hz, <u>C</u>HPh), 89.6 (dq, *J* = 190.9, 32.1 Hz, <u>C</u>F), 122.5 (qd, *J* = 280.8, 26.8 Hz, <u>C</u>F_3). ^{19}F NMR (470 MHz, $CDCl_3$) δ -76.33 (dd, *J* = 11.4, 6.1 Hz), -138.13 (ddq, J = 45.2, 22.4, 11.4 Hz, F). MS (GC-MS, EI), m/z, ($I_{rel.}$, %) D1+D2: 302 $[M]^+$ (27), 201 (100), 165 (72), 82 (16.7). HRMS (MALDI) (D1+D2) m/z calcd for $C_{15}H_{12}ClF_4$ $[M+H]^+$ 303.0558, found 303.0560.

*1-(4-Chlorophenyl)-2,3,3,3-tetrafluoro-1-(4-methoxyphenyl)propane (**2zc**).* Obtained as a mixture of diastereomers **D1***(1SR/2RS)* and **D2***(1RS/2RS)*. Yield 20 mg, 20 %. Colorless oil. Signals of **2zc-**

D1*(1SR/2RS)* and **2zc-D2***(1RS/2RS)* coincide: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19 – 7.29 (m, 6H), 6.85 (d, *J* = 8.6 Hz, 2H), 5.30 (m, 1H, C<u>H</u>F), 4.34 (dd, $J_{H\text{–}F}$ = 22.7 Hz, *J* = 5.6 Hz, 1H, C<u>H</u>Ph), 3.77 (s, 3H). ^{19}F NMR (470 MHz, $CDCl_3$) δ -76.24 (dd, *J* = 11.5, 6.3 Hz), -200.57 (m, F). **2zc-D2***(1RS/2RS)*: ^{19}F NMR (470 MHz, $CDCl_3$) δ -76.28 (dd, *J* = 11.0, 6.3 Hz), -200.79 (m, F). MS (GC-MS, EI), m/z, ($I_{rel.}$, %) D1+D2: 332 $[M]^+$ (29), 231 (35), 165 (31), 125 (100), 98 (10). HRMS (MALDI) (D1+D2) m/z calcd for $C_{16}H_{14}ClF_4O$ $[M+H]^+$ 333.0664, found 333.0668. $J_{H\text{–}F}$ = Hz

*1,1,1,2-Tetrafluoro-3-(4-methoxyphenyl)-3-phenylpropane (**2zd**)*. Obtained as a mixture of diastereomers **D1***(1SR/2RS)* and **D2***(1RS/2RS)*. Yield 80 mg, 91 %. Colorless oil. **2zd-D1***(1SR/2RS)*: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 – 7.35 (m, 7H), 6.88 (d, *J* = 8.6 Hz, 2H), 5.37 (ddq, $J_{H\text{–}F}$ = 45.5 Hz, *J* = 6.9, 6.2 Hz, 1H, C<u>H</u>F), 4.39 (dd, $J_{H\text{–}F}$ = 21.5 Hz, *J* = 6.9 Hz, 1H, C<u>H</u>Ph), 3.79 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (selected signals) 49.8 (d, *J* = 19.2 Hz, <u>C</u>HPh), 55.1 (OCH_3), 90.6 (dq, *J* = 190.0, 31.9 Hz, <u>C</u>F), 114.0, 122.8 (qd, *J* = 280.6, 26.3Hz, <u>C</u>F_3), **(D1+D2)**: 127.3, 127.4, 128.0, 128.6, 128.9, 129.2, 129.8, 129.9, 130.8, 130.9, 138.3, 158.8, 158.9. ^{19}F NMR (470 MHz, $CDCl_3$) δ -76.32 (dd, *J* = 11.0, 6.2 Hz), -118.3 (ddq, J = 45.5, 21.5, 11.0 Hz, F). **2zd-D2***(1RS/2RS)*: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 – 7.35 (m, 7H), 6.87 (d, J = 8.6 Hz, 2H), 5.37 (ddq, *J* = 45.5, 6.9, 6.2 Hz, 1H, C<u>H</u>F), 4.39 (dd, *J* = 21.5, 6.9 Hz, 1H, C<u>H</u>Ph), 3.78 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (selected signals) 49.7 (d, *J* = 19.2 Hz, <u>C</u>HPh), 55.2 (OCH_3), 89.9 (dq, *J* = 190.0, 31.9 Hz, <u>C</u>F), 114.2, 122.8 (qd, *J* = 280.6, 26.3Hz, <u>C</u>F_3). ^{19}F NMR (470 MHz, $CDCl_3$) δ -76.22 (dd, *J* = 11.0, 6.2 Hz), -117.0 (ddq, J = 45.5, 21.5, 11.0 Hz, F). MS (GC-MS, EI), m/z, ($I_{rel.}$, %) D1+D2: 298 $[M]^+$ (28), 197 (100), 182 (8), 165 (17), 153 (18). HRMS (MALDI) (D1+D2) m/z calcd for $C_{16}H_{15}F_4O$ $[M+H]^+$ 299.1054, found 299.1050.

*1,1,1,2-Tetrafluoro-3,3-bis(4-methoxyphenyl)propane (**2ze**)*. Yield 57 mg, 58 %. Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (m, 4H), 6.86 (d, *J* = 7.5 Hz, 4H), 5.37 (ddq, $J_{H\text{–}F}$ = 45.3 Hz, *J* = 6.0, 5.9 Hz, 1H, C<u>H</u>F), 4.34 (dd, $J_{H\text{–}F}$ = 22.2 Hz, *J* = 6.2 Hz, 1H, C<u>H</u>Ph), 3.78 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ

48.8 (d, J = 19.2 Hz, <u>C</u>HAr), 55.1 (OCH_3), 55.2 (OCH_3), 89.9 (dq, J = 190.0, 31.5 Hz, <u>C</u>F), 114.0, 114.2, 122.7 (qd, J = 281.0, 26.6 Hz, <u>C</u>F_3), 129.1, 129.8, 130.2, 131.3, 158.7, 158.8. ^{19}F NMR (470 MHz, $CDCl_3$) δ -76.20 (dd, J = 11.0, 6.0 Hz), -117.5 (ddq, J = 45.3, 22.2, 11.0 Hz, F). MS (GC-MS, EI), m/z, ($I_{rel.}$, %): 328 $[M]^+$ (25), 225 (36), 197 (21), 152 (11), 121 (100). HRMS (MALDI) (D1+D2) m/z calcd for $C_{17}H_{17}F_4O_2$ $[M+H]^+$ 329.1159, found 329.1161.

*1,1,1,2-Tetrafluoro-3-(4-methoxyphenyl)-3-(3,4-dimethoxyphenyl)propane (**2zf**)*. Obtained as a mixture of diastereomers **D1***(1SR/2RS)* and **D2***(1RS/2RS)*. Yield 30 mg, 28 %. Colorless oil. **2zf-D1***(1SR/2RS)*: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 – 7.24 (m, 2H), 6.77 – 6.90 (m, 5H), 5.29 (dquintet, J_{H-F} = 45.7 Hz, J = 6.4, 1H, C<u>H</u>F), 4.31 (dd, J_{H-F} = 22.8 Hz, J = 6.4 Hz, 1H, C<u>H</u>Ar_2), 3.84 (s, 6H), 3.78 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (selected signals) 49.1 (d, J = 19.7 Hz, <u>C</u>HAr_2), 55.2 (OCH_3), 55.8 (OCH_3), 55.9 (OCH_3), 90.7 (dq, J = 190.0, 31.7 Hz, <u>C</u>F), **(D1+D2)**: 111.2, 111.4, 111.6, 112.4, 114.0, 114.2, 120.1, 120.8, 122.6 (qd, J = 280.6, 26.7 Hz, <u>C</u>F_3), 129.1, 129.8, 130.1, 130.7, 131.1 d (C J_{C-F} = 4.5 Hz), 131.9 d (J_{C-F} J = 3.6 Hz), 148.3 d (J_{C-F} J = 2.7 Hz), 148.9, 149.1, 158.8 d (J_{C-F} J = 2.7 Hz). ^{19}F NMR (470 MHz, $CDCl_3$) δ -76.19 (dd, J = 11.4, 6.4 Hz), -200.32 (ddq, J = 45.7, 22.8, 11.4 Hz, F). MS (GC-MS, EI), m/z, ($I_{rel.}$, %) D1+D2: 358.2 $[M]^+$ (27), 257.1 (100). **2zf-D2***(1RS/2RS)*: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 – 7.24 (m, 2H), 6.77 – 6.90 (m, 5H), 5.30 (dquintet, J_{H-F} = 45.7 Hz, J = 6.4, 1H, C<u>H</u>F), 4.31 (dd, J_{H-F} = Hz 22.8, J = 6.4 Hz, 1H, C<u>H</u>Ar_2), 3.85 (s, 6H), 3.78 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (selected signals) 49.2 (d, J = 19.7 Hz, <u>C</u>HAr_2), 55.2 (OCH_3), 55.8 (OCH_3), 55.9 (OCH_3), 90.8 (dq, J = 190.0, 31.7 Hz, <u>C</u>F), ^{19}F NMR (470 MHz, $CDCl_3$) δ -76.29 (dd, J = 11.4, 6.4 Hz), -200.83 (ddq, J = 45.7, 22.8, 11.4 Hz, F). HRMS (MALDI) (D1+D2) m/z calcd for $C_{18}H_{19}F_4O_3$ $[M+H]^+$ 359.1265, found 359.1261.

*2-Chloro-1,1,1-trifluoro-3,3-bis(2,5-dimethylphenyl)propane (**2zg**)*. Obtained in mixture with compounds **2e** in ratio **2e** : **2zg** 9 : 1 in a whole yield 80 mg, 90 %. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.81 – 7.24 (m, 6H), 4.96 (m, 1H, C<u>H</u>CF_3), 4.50 (d, J = 8.1 Hz, 1H, C<u>H</u>Ar_2), 2.25 (s, 3H), 2.24 (s, 3H). ^{19}F NMR (470 MHz,

$CDCl_3$) δ -70.45 (d, *J* = 6.3 Hz). HRMS (MALDI) m/z calcd for $C_{19}H_{21}ClF_3$ $[M+H]^+$ 341.1278, found 341.1282.

*2-Bromo-1,1,1-trifluoro-3,3-bis(2,5-dimethylphenyl)propane (**2zh**).* Yield 51 mg, 44 %. Colorless crystal. M.p. 108-110 °C. Single crystal suitable for X-ray diffraction was obtained by slow evaporation of a diluted solution of **2zh** in EtOAc. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.81 – 7.24 (m, 6H), 4.93 (m, 1H, C<u>H</u>CF_3), 3.77 (d, *J* = 9.8 Hz, 1H, C<u>H</u>Ar_2), 2.39 (s, 3H), 2.36 (s, 3H), 2.33 (s, 3H), 2.29 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 19.2, 19.9, 21.2, 21.4, 43.5, 51.1 (q, *J* = 29.0 Hz, <u>C</u>HBr), 55.2, 113.7, 114.0, 124.2 (q, *J* = 277.5 Hz, CF_3), 127.7, 127.9, 128.1, 128.5, 129.6, 129.9, 130.6, 130.9, 137.2, 138.7. ^{19}F NMR (470 MHz, $CDCl_3$) δ -67.60 (d, *J* = 6.3 Hz). MS (GC-MS, EI), m/z, ($I_{rel.}$, %): 386.2 $[M]^+$ (11), 384.2 $[M]^+$ (11), 223.2 (100), 208.2 (11), 193.2 (11). HRMS (MALDI) m/z calcd for $C_{19}H_{21}BrF_3$ $[M+H]^+$ 385.0773, found 385.0768.

*(E-/Z)-3,3,3-Trifluoro-1-(3,4-dimethylphenyl)-1-phenylpropene (**3c**).* Yield 24 mg, 87 %. Yellowish oil. Mixture of isomers *Z*- and *E*-. ***Z*-3c**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33-7.40 (m, 3H), 7.14-7.27 (m, 2H), 6.95-7.10 (m, 3H), 6.07 (q, *J* = 8.5 Hz, 1H, C<u>H</u>=), 2.27 (s, 3H), 2.24 (s, 3H), ^{19}F NMR (470 MHz, $CDCl_3$) δ -56.43 (d, *J* = 8.7 Hz). ***E*-3c**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33-7.40 (m, 3H), 7.14-7.27 (m, 2H), 6.95-7.10 (m, 3H), 6.10 (q, *J* = 8.5 Hz, 1H, C<u>H</u>=), 2.31 (s, 3H), 2.26 (s, 3H). ^{19}F NMR (470 MHz, $CDCl_3$) δ -56.60 (d, *J* = 8.3 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) (for mixture of isomers):19.5, 19.6, 19.7, 19.8, 114.4 (q, J = 33.5 Hz), 115.0 (q, *J* = 33.5 Hz), 123.9 (q, *J* = 268.5 Hz), 123.2 (q, *J* = 268.5 Hz), 125.5, 126.7, 127.9, 128.0, 128.3, 128.4, 129.0, 129.1, 129.2, 129.7, 130.2, 134.8, 136.2, 136.7, 137.0, 137.5, 137.7, 138.3, 140.6, 152.5 (q, *J* = 5.6 Hz), 152.7 (q, *J* = 5.6 Hz). HRMS (MALDI) m/z calcd for $C_{17}H_{16}F_3$ $[M+H]^+$ 277.1199, found 277.1203.

*(E-/Z)-3,3,3-Trifluoro-1-(2,4,5-trimethylphenyl)-1-phenylpropene (**3f**).* Yield 21 mg, 74%. Yellowish oil. Mixture of isomers *Z*- and *E*-. ***Z*-3f**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27-7.35 (m, 5H), 6.92 - 6.99 (m, 2H),

6.24 (q, *J* = 8.0 Hz, 1H, CH=), 2.27 (s, 3H), 2.26 (s, 3H), 2.24 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -56.58 (d, *J* = 8.0 Hz). ***E*-3f**: ^{1}H NMR (500 MHz, $CDCl_3$) δ7.27-7.35 (m, 5H), 6.92 - 6.99 (m, 2H), 5.77 (q, *J* = 8.0 Hz, 1H, CH=), 2.24 (s, 3H), 1.99 (s, 3H), 1.98 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.12 (d, *J* = 8.0 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) (for mixture of isomers): 18.9, 19.1, 19.2, 19.3, 19.5, 19.6, 115.4 (q, *J* = 33.5 Hz), 117.5 (q, *J* = 33.5 Hz), 122.9 (q, *J* = 268.5 Hz), 123.2 (q, *J* = 268.5 Hz), 127.0, 127.9, 128.5, 128.6, 128.8, 129.3, 130.2, 130.6, 131.3, 132.1, 132.8, 132.9, 133.3, 133.7, 133.8, 136.5, 137.0, 137.9, 138.7, 138.8, 152.5 (q, *J* = 5.5 Hz), 152.6 (q, *J* = 5.5 Hz). HRMS (MALDI) m/z calcd for $C_{18}H_{18}F_3$ $[M+H]^+$ 291.1355, found 291.1353.

(E-/Z)-1,1,1-Trifluoro-3-(4-methoxylphenyl)-3-(3,4-dimethoxyphenyl)propene ***(3q)***. Yield 33 mg, 96 %. Yellowish oil. Mixture of *Z*- and *E*- isomers: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.82 (s, 3H, OMe), 3.85 (s, 3H, OMe), 3.89 (s, 3H, OMe), 3.92 (s, 3H, OMe), 5.99 (q, *J* = 8.4 Hz, 1H, CH=,), 6.75-6.92 (m, $5H_{arom}$,), 7.17-7.22 (m, $2H_{arom}$). ^{13}C NMR (125 MHz, $CDCl_3$), *δ*, ppm: 55.2, 55.3, 55.8, 55.8, 55.9, 110.5, 110.7, 111.0, 112.6, 112.7, 113.1 (q, *J* = 33.4 Hz), 113.3 (q, *J* = 33.4 Hz), 113.4, 113.8, 121.5, 122.1, 123.3 (q, *J* = 268.5 Hz), 123.4 (q. *J* = 268.5 Hz), 129.5, 129.6, 130.0, 130.7, 132.7, 133.4, 148.4, 148.7, 149.2, 150.2, 151.80 (q, *J* = 5.4 Hz), 152.0 (q, *J* = 5.4 Hz), 159.8, 160.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -55.03, -55.05. HRMS (MALDI) m/z calcd for $C_{18}H_{18}F_3O_3$ $[M+H]^+$ 339.1203, found 339.1195.

2-Bromo-3,3,3-trifluoro-3-(4-methoxyphenyl)propan-1-ol *(**4**)*. Obtained as a mixture of diastereomers **D1** and **D2** (unknown assignment). Yield 32 mg, 36 % (see Scheme 4). Colorless oil. **4-D1**(unknown assignment*)*: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 – 7.32 (m, 2H), 6.91 – 6.93 (m, 2H), 5.05 (d, *J* = 7.0 Hz, 1H, CHOH), 4.44 (quintet, *J* = 7.0 Hz, 1H, CHBr), 3.82 (s, 3H), 2.43 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (selected signals) 51.3 (q, *J* = 29.0 Hz, CBr), 55.3 (OCH_3), 73.0 (CHOH), 123.4 (qd, *J* = 277.5, CF_3), **(D1+D2)**: 113.8, 114.0, 127.2, 128.4, 131.0, 131.2, 159.8, 160.0. ^{19}F NMR (470 MHz, $CDCl_3$) δ -67.48 (d, *J* = 7.0 Hz). MS (GC-MS, EI), m/z, ($I_{rel.}$, %) D1+D2: 300.1 $[M+2]^+$ (5), 298$[M]^+$ (5), 137.2

(100), 109.2 (13), 94.2(11), 77(11). **4-D2** (unknown assignment): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 – 7.32 (m, 2H), 6.91 – 6.93 (m, 2H), 5.11 (d, *J* = 7.0 Hz, 1H, C<u>H</u>OH), 4.34 (quintet, *J* = 7.0 Hz, 1H, C<u>H</u>Br), 3.81 (s, 3H), 2.43 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (selected signals) 54.9 (q, *J* = 29.0 Hz, <u>C</u>Br), 55.2 (O<u>C</u>H_3), 70.3 (<u>C</u>HOH), 123.3 (qd, *J* = 277.5, <u>C</u>F_3). ^{19}F NMR (470 MHz, $CDCl_3$) δ -69.18 (d, *J* = 7.0 Hz). HRMS (MALDI) (D1+D2) m/z calcd for $C_{10}H_{11}BrF_3O_2$ $[M+H]^+$ 298.9889, found 298.9879.

*1-Chloro-1,1,2-trifluoro-3-(4-methoxyphenyl)-3-phenylpropane (**6a**).* Obtained as a mixture of diastereomers **D1** and **D2** (unknown assignment). Yield 55 mg, 58 %. Yellowish oil. **6a-D1**(unknown assignment): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 – 7.34 (m, 7H), 6.85 (d, *J* = 8.6 Hz, 2H), 5.36 (dq, $J_{H\text{–}F}$ = 45.4 Hz, *J* = 6.8 Hz, 1H, C<u>H</u>F), 4.48 (dd, $J_{H\text{–}F}$ = 19.8 Hz, *J* = 6.6 Hz, 1H, C<u>H</u>Br), 3.78 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (selected signals) 50.4 (d, J = 20.1 Hz, <u>C</u>HPh), 55.2 (O<u>C</u>H_3), **(D1+D2)**: 93.4 (dt, *J* = 194.0, 27.2 Hz, <u>C</u>F), 114.0, 114.2, 127.2, 127.3, 128.1, 128.6, 128.7, 128.8, 129.2, 130.0, 130.1, 131.2, 131.3, 132.9, 138.5, 158.8. ^{19}F NMR (470 MHz, $CDCl_3$) δ -60.67 (ddd, J = 170.6, 16.3, 6.8 Hz), -127.73 (ddt, *J* = 45.4, 19.8, 16.3 Hz). MS (GC-MS, EI), m/z, ($I_{rel.}$, %) D1+D2: 316 $[M+2]^+$ (5), 314 $[M]^+$ (20), 197 (100), 182 (8), 165 (15), 153(15). **6a-D2** (unknown assignment): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 – 7.34 (m, 7H), 6.85 (d, *J* = 8.6 Hz, 2H), 5.36 (dq, $J_{H\text{–}F}$ = 45. Hz 4, *J* = 6.8 Hz, 1H, C<u>H</u>F), 4.49 (dd, $J_{H\text{–}F}$ = 19.8 Hz, *J* = 6.6 Hz, 1H, C<u>H</u>Br), 3.79 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (selected signals) 50.3 (d, *J* = 20.1 Hz, <u>C</u>HPh), 55.2 (O<u>C</u>H_3). ^{19}F NMR (470 MHz, $CDCl_3$) δ -63.08 (ddd, J = 170.6, 16.3, 6.8 Hz), -126.42 (ddt, *J* = 45.4, 19.8, 16.3 Hz). HRMS (MALDI) (D1+D2) m/z calcd for $C_{16}H_{15}ClF_3O$ $[M+H]^+$ 315.0758, found 315.0755.

*1-Chloro-1,1,2-trifluoro-3-bis(4-methoxyphenyl)propane (**6b**).* Yield 99 mg, 96 %. Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 – 7.24 (m, 8H), 6.85 (d, *J* = 10.9 Hz, 2H), 5.36 (dq, $J_{H\text{–}F}$ = 51.0 Hz, *J* = 8.9 Hz, 1H, C<u>H</u>F), 4.43 (dd, $J_{H\text{–}F}$ = 27.0 Hz, *J* = 8.9 Hz, 1H, C<u>H</u>Br), 3.78 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 49.5 (d, J = 20.0 Hz, <u>C</u>HAr), 55.2 (O<u>C</u>H_3), 55.2 (O<u>C</u>H_3), 93.5 (dt, *J* = 193.6, 27.2 Hz, <u>C</u>F), 113.9, 114.2, 129.1, 129.9, 130.5, 131.6, 131.7, 132.2 m (<u>C</u>F_2Cl), 158.71. ^{19}F NMR (470 MHz, $CDCl_3$) δ -60.92 (ddd, J = 170.0, 16.5, 8.9 Hz), -60.93 (ddd, J = 170.0, 16.5, 8.9 Hz), -191.58 (ddt, *J* = 51.0, 21.5, 16.5 Hz). HRMS (MALDI) m/z calcd for $C_{17}H_{17}ClF_3O_2$ $[M+H]^+$ 345.0864, found 345.0866.

*(E-/Z)-3-(4-Chlorophenyl)-2-fluoro-1-phenylprop-2-en-1-one (7**a**).*[30a] Obtained as a mixture of *Z/E*-isomers with Z-/E- ratio 16 : 1 in a yield of 60 mg, 63 %. Colorless solid, m. p. 75-77 °C. *Z*-**7a**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.3 Hz, 2H), 7.64 (d, *J* = 7.9 Hz, 2H), 7.61 (t, *J* = 7.3 Hz, 1H), 7.50 (t, 2H, *J* = 7.3 Hz), 7.40 (d, *J* = 7.9 Hz, 2H), 6.83 d (1H, C=C<u>H</u>, *J* 35.7 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 118.5 (d, *J* = 5.8 Hz), 128.5, 129.2, 129.3 (d, *J* = 3.7 Hz), 131.7 (d, *J* = 8.5 Hz), 133.0, 136.0 (d, *J* = 3.7 Hz), 136.0, 154.7 (d, *J* = 272.6 Hz, CF), 187.5 (d, *J* = 29 Hz, CPh). ^{19}F NMR (470 MHz, $CDCl_3$) δ -119.41 (d, *J* = 35.7 Hz, C<u>F</u>). MS (GC-MS, EI), m/z, ($I_{rel.}$, %) 260.1 $[M]^+$ (70), 225.2 (38), 205.2 (34), 120.2 (19), 105.1 (100), 77.2 (82). *E*-**7a**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.87 d (1H, C<u>H</u>F, *J* = 35.7 Hz). ^{19}F NMR (470 MHz, $CDCl_3$) δ -120.28 d (C<u>F</u>, *J* = 35.7 Hz). HRMS (MALDI) m/z calcd for $C_{15}H_{11}ClFO$ $[M+H]^+$ 261.0477, found 261.0481.

*(Z)-3-(4-Chlorophenyl)-2-fluoro-1-(4-methoxyphenyl prop-2-en-1-one (7**b**).* Yield 68 mg, 65 %. Colorless solid m. p. 82-84 °C. *Z*-**7b**:^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.7 Hz, 2H), 7.64 (d, *J* = 8.5 Hz, 2H), 7.40 (d, *J* = 8.5 Hz, 2H), 6.98 (d, *J* = 8.7 Hz, 2H), 6.83 (d, $J_{H\text{–}F}$ = 36.6 Hz, 1H, C=C<u>H</u>), 3.90 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 55.5 (OCH_3), 113.8, 117.2 (d, *J* = 5.4 Hz), 128.5 (d, *J* = 1.8 Hz), 129.1, 130.07 (d, *J* = 4.0 Hz), 131.7 (d, *J* = 8.5 Hz), 132.0 (d, *J* = 4.0 Hz), 135.6 (d, *J* = 3.6 Hz), 155.3 (d , *J* = 274.3 Hz, CF), 163.8, 185.7 (d, *J* = 29 Hz). ^{19}F NMR (470 MHz, $CDCl_3$) δ -118.09 (d, *J* = 36.6 Hz, C<u>F</u>). MS (GC-MS, EI), m/z, ($I_{rel.}$, %) 290.1 $[M]^+$ (39), 270.1 (29), 135.1 (100), 107.1 (11), 77.2 (24). HRMS (MALDI) m/z calcd for $C_{16}H_{13}ClFO_2$ $[M+H]^+$ 291.0583, found 291.0580.

*Cation **A8***. ^{1}H NMR (500 MHz, FSO_3H) δ 8.44 (broad m, $1H_{ortho-}$), 8.29 (broad m, $1H_{ortho-}$),8.04 d (1H, C^1H, *J*= 10.9 Hz), 7.47 (broad s, $2H_{meta-}$), 5.81 (dq, 1H, C^2H, *J*= 10.9 Hz, *J*= 5.3 Hz), 4.59 (s, 3H, OMe).

^{13}C NMR (125 MHz, FSO_3H) δ 38.1 q (C^2, ^2J = 37 Hz), 62.6 (OMe), ~120 (broad signal, C_{meta-}), 122.7 (q, CF_3, J = 276 Hz), ~127 (broad signal, C_{ortho-}), 134.8 (C_{ipso-}), 164.5 ($^+C^1$), 189.2 (C_{para-}). ^{19}F NMR (470 MHz, FSO_3H) δ -73.28 (d, CF_3, J = 5.3 Hz).

Supporting Information

^{1}H, ^{13}C, ^{19}F NMR spectra of compounds, details of DFT calculations, X-ray data.

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