Supporting Information

Brominated CF_3-Allyl Alcohols as Multicentered Electrophiles in TfOH Promoted Reactions with Arenes

Anna N. Kazakova,[1] Roman O. Iakovenko,[1] Irina A. Boyarskaya,[1] Alexander Yu. Ivanov,[2] Margarita S. Avdontceva,[3] Andrei A. Zolotarev,[3] Taras L. Panikorovsky,[3] Valentine G. Nenajdenko,[4]* Aleksander V. Vasilyev[1,5] *

[1]*Department of Organic Chemistry, Institute of Chemistry, Saint Petersburg State University, Universitetskaya nab., 7/9, Saint Petersburg , 199034, Russia.*
[2]*Center for Magnetic Resonance, Research park, St. Petersburg State University, Universitetskiy pr. 26, Saint Petersburg, Petrodvoretz, 198504 , Russia.*
[3]*Center for X-ray Diffraction Studies Research park, St. Petersburg State University, Universitetskiy pr. 26, Saint Petersburg, Petrodvoretz, 198504 , Russia.*
[4]*Department of Chemistry, Moscow State University, Vorobievy Gory, 1, Moscow, 119899, Russia.*
[5]*Department of Chemistry, Saint Petersburg State Forest Technical University, Institutsky per., 5, Saint Petersburg , 194021, Russia.*

*Corresponding authors: V.G. Nenajdenko: e-*mail: nenajdenko@org.chem.msu.ru;*
A.V. Vasilyev; e-mails: *aleksvasil@mail.ru; a.vasilyev@spbu.ru*

Table of Contents:

General Information

The NMR spectra of solutions of compounds in $CDCl_3$ were recorded on 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). NMR experiments in the superacids TfOH at room temperature or - 20° C were performed with the same NMR spectrometer. NMR spectra in TfOH were referenced to the signal of CH_2Cl_2 added as internal standard: δ 5.30 ppm for ^1H NMR spectra, and δ 53.52 ppm for ^{13}C NMR spectra. HRMS was carried out at instruments Bruker maXis HRMS-ESI-QTOF and Varian 902-MS MALDI Mass Spectrometer. Chromato-mass-spectrometry data were obtained at Shimadzu QP-2010 Ultra with a SPB-1 SULFUR capillary column (30 m × 0.32 mm), thickness of the stationary phase 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 petroleum ether-ethyl acetate mixture eluation.

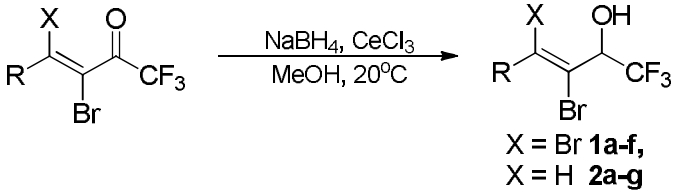
Single crystal X-ray analysis was performed at single crystal diffractometer Agilent Technologies (Oxford Diffraction) «Supernova». A suitable crystal was selected and studied on the diffractometer. The crystal was kept at 100(2) K during data collection. Using Olex2[1] the structure was solved with the ShelXS[2] structure solution program using Direct Methods and refined with the ShelXL refinement package using Least Squares minimisation. CCDC 1498476 – (*Z*-**5a**), CCDC 1418365 – (*Z*-**5c**), CCDC 1413018 – (*Z*-**5i**), CCDC 1498617 – (**6d**), CCDC 1498726 – (**8o**), CCDC 1413020 – (**8u**), CCDC 1413019 – (**10b**) contain 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 2003 program packages.[3] 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. Gibbs free energies were calculated for 25°C. Solvent-phase calculations used the Polarizable Continuum Model (PCM).

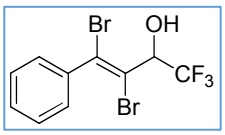
Preparation and characterization of starting materials

4-Aryl-3,4-dibromo- (or 3-bromo-) 1,1,1-trufluorobut-3-en-2-ols 1a-f, 2a-g were synthesized by modification of the known procedure.[4]

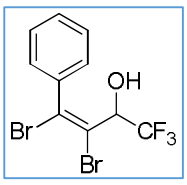


To a stirred mixture of substituted *E*-, *Z*-4-aryl-3,4-dibromo-1,1,1-trufluorobut-3-en-2-ones or *Z*-4-aryl-3-bromo-1,1,1-trufluorobut-3-en-2-ones (1 mmol) and cerium chloride heptahydrate (1.1 mmol) in methanol (2 ml), $NaBH_4$ (1.1 mmol) was added at 0°C. The mixture was stirred at room temperature for 10 min, and then $NaBH_4$ (0.55 mmol) was added at 0°C. The mixture was stirred at room temperature for another 10 min. For 3,4-dibromo-4-aryl-1,1,1-trufluorobut-3-en-2-ones this procedure of adding $NaBH_4$ (0.55 mmol) repeated one more time. Then aqueous NH_4Cl solution was added, the mixture was extracted with Et_2O. The combined extracts were dried over Na_2SO_4 and the solvents were removed under reduced pressure. The residue was chromatographed on a silica gel column, using petroleum ether or petroleum ether-EtOAc mixtures (8:2) as an eluent.

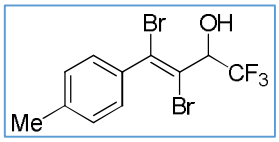
(*E*)-3,4-Dibromo-1,1,1-trifluoro-4-phenylbut-3-en-2-ol (*E*-1a): Obtained in mixture with alcohol Z-**1a** (*E*-**1a** : *Z*-**1a**, 1:2). Pale yellow oil. The reaction scale is 500 mg (1.4 mmol) mixture of *E*-/*Z*-isomers 3,4-dibromo-1,1,1-trifluoro-4-phenylbut-3-en-2-ones, isolated amount is 422 mg, 84% yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 2.94 m (1H, OH), 5.49 dq (1H, C^2H, ^3J 11.9 Hz, $^3J_{H\text{-}F}$ 6.0 Hz), 7.35-7.45 m ($5H_{Ph}$). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 72.4 q (C^2, $J_{C\text{-}F}$ 33.3 Hz), 116.4 (C^3), 124.5 (C^4), 125.8 q (C^1, $J_{C\text{-}F}$ 284.2 Hz), 128.6, 128.7, 129.7, 139.7. ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: -75.69 m (CF_3). HRMS (ESI): $C_{10}H_7Br_2F_3OAg$ found 464.7868 $[M+Ag]^+$; calcd. 464.7861.



(*Z*)-3,4-Dibromo-1,1,1-trifluoro-4-phenylbut-3-en-2-ol (*Z*-1a): ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 2.79 m (1H, OH), 4.64 dq (1H, C^2H, ^3J 11.6 Hz, $^3J_{H\text{-}F}$ 5.9 Hz), 7.31-7.43 m ($5H_{Ph}$). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 70.5 q (C^2, $J_{C\text{-}F}$ 33.5 Hz), 122.3 d (C^3, $J_{C\text{-}F}$ 0.9 Hz), 123.0 q (C^1, $J_{C\text{-}F}$ 284.6 Hz), 128.3, 129.2, 130.0, 132.9 (C^4), 138.1. ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: -74.82 t (CF_3, $J_{H\text{-}F}$ 5.9 Hz). HRMS (ESI): $C_{10}H_7Br_2F_3OAg$ found 464.7868 $[M+Ag]^+$; calcd. 464.7861.

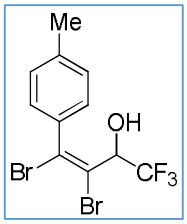


(*E*)-3,4-Dibromo-1,1,1-trifluoro-4-(4-methylphenyl)but-3-en-2-ol (*E*-1b): Obtained in



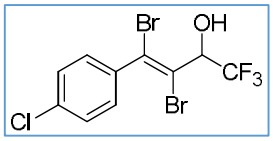
mixture with alcohol *Z*-**1b** (*E*-**1b** : *Z*-**1b**, 1:3.7). Pale yellow oil. The reaction scale is 200 mg (0.54 mmol) mixture of *E*-/*Z*-isomers 3,4-dibromo-1,1,1-trifluoro-4-(4-methylphenyl)but-3-en-2-ones, isolated amount is 202 mg, 98% yield ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 2.39 s (3H, CH_3), 2.99 d (1H, OH, ^{3}J 10.5 Hz), 5.49 dq (1H, $C^{2}H$, ^{3}J 12.0 Hz, $^{3}J_{H\text{-}F}$ 6.1 Hz), 7.23-7.33 m ($4H_{arom.}$). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 21.6 (CH_3), 72.5 q (C^{2}, $J_{C\text{-}F}$ 33.4 Hz), 115.9 (C^{3}), 123.0 q (C^{1}, $J_{C\text{-}F}$ 284.6 Hz), 128.6, 129.3 (C^{4}), 129.4, 136.8, 140.0. ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: -75.69 d (CF_3, $J_{H\text{-}F}$ 6.1 Hz). HRMS (ESI): $C_{11}H_9Br_2F_3OAg$ found 478.8028 $[M+Ag]^{+}$; calcd. 478.8018.

(*Z*)-3,4-Dibromo-1,1,1-trifluoro-4-(4-methylphenyl)but-3-en-2-ol (*Z*-1b):



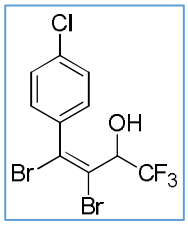
^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 2.39 s (3H, CH_3), 2.84 d (1H, OH, ^{3}J 10.5 Hz), 4.66 dq (1H, $C^{2}H$, ^{3}J 11.7 Hz, $^{3}J_{H\text{-}F}$ 6.0 Hz), 7.19-7.23 m ($4H_{arom.}$). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 21.5 (CH_3), 70.5 q (C^{2}, $J_{C\text{-}F}$ 33.6 Hz), 121.9 q (C^{3}, $J_{C\text{-}F}$ 1.0 Hz), 123.0 q (C^{1}, $J_{C\text{-}F}$ 284.6 Hz), 128.2, 129.8, 133.3 q (C^{4}, $J_{C\text{-}F}$ 0.8 Hz), 135.2, 140.3. ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: -74.81 d (CF_3, $J_{H\text{-}F}$ 6.0 Hz). HRMS (ESI): $C_{11}H_9Br_2F_3OAg$ found 478.8028 $[M+Ag]^{+}$; calcd. 478.8018.

(*E*)-3,4-Dibromo-4-(4-chlorophenyl)-1,1,1-trifluorobut-3-en-2-ol (*E*-1c): Obtained in

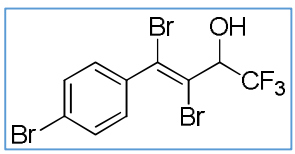


mixture with alcohol Z-**1c** (*E*-**1c** : *Z*-**1c**, 1:3). Pale yellow oil. The reaction scale is 200 mg (0.51 mmol) mixture of *E*-/*Z*-isomers 3,4-dibromo-1,1,1-trifluoro-4-(4-chlorophenyl)but-3-en-2-ones, isolated amount is 196 mg, 98% yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 3.01 d (1H, OH, ^{3}J 9.8 Hz), 5.47 dq (1H, $C^{2}H$, ^{3}J 11.8 Hz, $^{3}J_{H\text{-}F}$ 6.0 Hz), 7.31 d ($2H_{arom.}$, ^{3}J 8.6 Hz), 7.40 d ($2H_{arom.}$, ^{3}J 8.6 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 72.4 q (C^{2}, $J_{C\text{-}F}$ 34.5 Hz), 117.1 (C^{3}), 120.6 q (C^{1}, $J_{C\text{-}F}$ 284.6 Hz), 123.2 (C^{4}), 129.1, 130.1, 135.8, 138.0. ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: -75.68 d (CF_3, $J_{H\text{-}F}$ 6.0 Hz). HRMS (ESI): $C_{10}H_6Br_2ClF_3OAg$ found 498.7487 $[M+Ag]^{+}$; calcd. 498.7471.

(*Z*)-3,4-Dibromo-4-(4-chlorophenyl)-1,1,1-trifluorobut-3-en-2-ol (*Z*-1c):



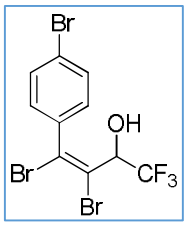
^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 2.89 d (1H, OH, ^{3}J 9.1 Hz), 4.59 dq (1H, $C^{2}H$, ^{3}J 11.5 Hz, $^{3}J_{H\text{-}F}$ 6.0 Hz), 7.26 d ($2H_{arom.}$, ^{3}J 8.5 Hz), 7.41 d ($2H_{arom.}$, ^{3}J 8.6 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 70.5 q (C^{2}, $J_{C\text{-}F}$ 33.5 Hz), 122.9 q (C^{1}, $J_{C\text{-}F}$ 284.6 Hz), 123.0 q (C^{3}, $J_{C\text{-}F}$ 1.1 Hz), 129.5, 129.7, 131.5 (C^{4}), 136.3, 136.5. ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: -74.84 d (CF_3, $J_{H\text{-}F}$ 6.0 Hz). HRMS (ESI): $C_{10}H_6Br_2ClF_3OAg$ found 498.7487 $[M+Ag]^{+}$; calcd. 498.7471.



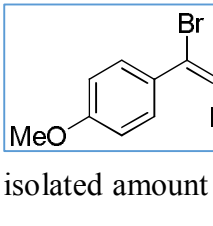
(*E*)-3,4-Dibromo-4-(4-bromophenyl)-1,1,1-trifluorobut-3-en-2-ol (*E*-1d): Obtained in mixture with alcohol Z-**1d** (*E*-**1d** : *Z*-**1d**, 1:2.8). Pale brown oil. The reaction scale is 200 mg (0.46 mmol) mixture of *E*-

/*Z*-isomers 3,4-dibromo-1,1,1-trifluoro-4-(4-bromophenyl)but-3-en-2-ones, isolated amount is 195 mg, 97% yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 2.94-2.96 m (1H, OH), 5.44-5.47 m (1H, C^2H), 7.24 d ($2H_{arom.}$, ^{3}J 8.6 Hz), 7.56 d ($2H_{arom.}$, ^{3}J 8.5 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 72.4 q (C^2, $J_{C\text{-}F}$ 33.2 Hz), 115.4 (C^3), 122.9 q (C^1, $J_{C\text{-}F}$ 284.5 Hz), 123.2 (C^4), 124.1, 130.3, 132.1, 138.5. ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: -75.69 d (CF_3, $J_{H\text{-}F}$ 6.0 Hz). HRMS (ESI): $C_{10}H_6Br_3F_3OAg$ found 542.6983 $[M+Ag]^+$; calcd. 542.6966.

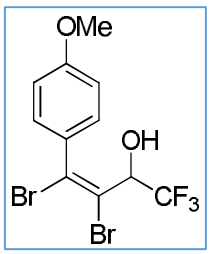
(*Z*)-3,4-Dibromo-4-(4-bromophenyl)-1,1,1-trifluorobut-3-en-2-ol (*Z*-1d): ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 2.82-2.83 m (1H, OH), 4.56 m (1H, C^2H), 7.19 d ($2H_{arom.}$, ^{3}J 8.5 Hz), 7.57 d ($2H_{arom.}$, ^{3}J 8.5 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 70.5 q (C^2, $J_{C\text{-}F}$ 33.6 Hz), 122.9 q (C^1, $J_{C\text{-}F}$ 284.5 Hz), 123.0 q (C^3, $J_{C\text{-}F}$ 1.0 Hz), 124.6, 129.9, 131.5 q (C^4, $J_{C\text{-}F}$ 0.9 Hz), 132.5, 136.9. ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: -74.84 d (CF_3, $J_{H\text{-}F}$ 5.8 Hz). HRMS (ESI): $C_{10}H_6Br_3F_3OAg$ found 542.6983 $[M+Ag]^+$; calcd. 542.6966.



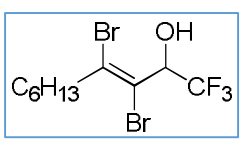
(*E*)-3,4-Dibromo-1,1,1-trifluoro-4-(4-methoxyphenyl)but-3-en-2-ol (*E*-1e): Obtained in mixture with alcohol *Z*-**1e** (*E*-**1e** : *Z*-**1e**, 1:2.5). Colorless oil. The reaction scale is 200 mg (0.52 mmol) mixture of *E*-/*Z*-isomers 3,4-dibromo-1,1,1-trifluoro-4-(4-methoxyphenyl)but-3-en-2-ones, isolated amount is 198 mg, 98% yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 3.01 d (1H, OH, ^{3}J 10.6 Hz), 3.84 s (3H, CH_3), 5.48 dq (1H, C^2H, ^{3}J 12.0 Hz, $^{3}J_{H\text{-}F}$ 6.1 Hz), 6.92 d ($2H_{arom.}$, ^{3}J 8.8 Hz), 7.33 d ($2H_{arom.}$, ^{3}J 8.8 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 55.5 (CH_3), 72.6 q (C^2, $J_{C\text{-}F}$ 33.2 Hz), 114.0, 115.7 (C^3), 123.0 q (C^1, $J_{C\text{-}F}$ 284.3 Hz), 124.8 (C^4), 130.4, 131.8, 160.5. ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: -75.66 d (CF_3, $J_{H\text{-}F}$ 6.1 Hz). HRMS (ESI): $C_{11}H_9Br_2F_3O_2Ag$ found 494.7981 $[M+Ag]^+$, calcd. 494.7967.



(*Z*)-3,4-Dibromo-1,1,1-trifluoro-4-(4-methoxyphenyl)but-3-en-2-ol (*Z*-1e): ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 2.87 d (1H, OH, ^{3}J 10.6 Hz), 3.84 s (3H, CH_3), 4.68 dq (1H, C^2H, ^{3}J 11.9 Hz, $^{3}J_{H\text{-}F}$ 6.0 Hz), 6.92 d ($2H_{arom.}$, ^{3}J 8.8 Hz), 7.25 d ($2H_{arom.}$, ^{3}J 8.8 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 55.6 (CH_3), 70.5 q (C^2, $J_{C\text{-}F}$ 33.4 Hz), 114.5, 121.9 q (C^3, $J_{C\text{-}F}$ 1.0 Hz), 123.0 q (C^1, $J_{C\text{-}F}$ 284.4 Hz), 129.9, 130.3, 133.3 q (C^4, $J_{C\text{-}F}$ 0.5 Hz), 160.7. ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: -74.76 d (CF_3, $J_{H\text{-}F}$ 6.0 Hz). HRMS (ESI): $C_{11}H_9Br_2F_3O_2Ag$ found 494.7981 $[M+Ag]^+$, calcd. 494.7967.

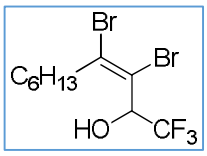


(*E*)-3,4-Dibromo-1,1,1-trifluorodec-3-en-2-ol (*E*-1f): Obtained in mixture with alcohol *Z*-**1f** (*E*-**1f** : *Z*-**1f**, 3.5:1). Colorless liquid. The reaction scale is 200 mg (0.55 mmol) mixture of *E*-/*Z*-isomers 3,4-dibromo-1,1,1-trifluorodec-3-en-2-ones, isolated amount is 180 mg, 89% yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm:

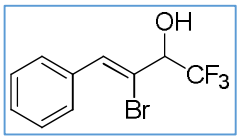


0.90 t (3H, CH_3, ^3J 6.7 Hz), 1.32-1.35 m (6H, CH_2), 1.58-1.64 m (2H, CH_2), 2.71-2.85 m (3H, CH_2, OH), 5.33 q (1H, C^2H, $^3J_{H\text{-}F}$ 6.1 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 14.1 (CH_3), 22.6 (CH_2), 27.2 (CH_2), 28.2 (CH_2), 31.6 (CH_2), 41.3 (CH_2), 72.3 q (C^2, $J_{C\text{-}F}$ 33.2 Hz), 114.5 q (C^3, $J_{C\text{-}F}$ 1.0 Hz), 123.5 q (C^1, $J_{C\text{-}F}$ 284.9 Hz), 130.2 (C^4). ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: -75.88 d (CF_3, $J_{H\text{-}F}$ 6.1 Hz). HRMS (ESI): $C_{10}H_{15}Br_2F_3OAg$ found 472.8421 $[M+Ag]^+$; calcd. 472.8487.

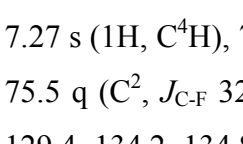
(*Z*)-3,4-dibromo-1,1,1-trifluorodec-3-en-2-ol (*Z*-1f): ^1H NMR ($CDCl_3$, 400 MHz) δ, ppm: 0.90 t (3H, CH_3, ^3J 6.7 Hz), 1.32-1.35 m (6H, CH_2), 1.58-1.64 m (2H, CH_2), 2.64 ddd (2H, CH_2, ^2J 8.9 Hz, ^3J 6.6 Hz, ^3J 3.8 Hz), 2.71-2.85 m (1H, OH), 4.88 q (1H, C^2H, $^3J_{H\text{-}F}$ 6.0 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 14.1 (CH_3), 22.6 (CH_2), 28.5 (CH_2), 28.7 (CH_2), 31.6 (CH_2), 39.0 (CH_2), 69.5 q (C^2, $J_{C\text{-}F}$ 33.4 Hz), 119.6 q (C^3, $J_{C\text{-}F}$ 0.9 Hz), 123.5 q (C^1, $J_{C\text{-}F}$ 284.9 Hz), 137.3 (C^4). ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: -76.11 d (CF_3, $J_{H\text{-}F}$ 6.0 Hz). HRMS (ESI): $C_{10}H_{15}Br_2F_3OAg$ found 472.8421 $[M+Ag]^+$; calcd. 472.8487.



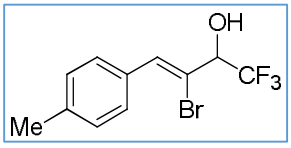
(*Z*)-3-Bromo-1,1,1-trifluoro-4-phenylbut-3-en-2-ol (2a):[5] pale yellow oil. The reaction scale is 288 mg (1.0 mmol) (*Z*)-3-bromo-1,1,1-trifluoro-4-phenylbut-3-en-2-one, isolated amount is 243 mg, 86% yield. ^1H NMR ($CDCl_3$, 400 MHz) δ, ppm: 2.88 d (1H, OH, ^3J 8.6 Hz), 4.70 dq (1H, C^2H, ^3J 8.6 Hz, $^3J_{H\text{-}F}$ 6.1 Hz), 7.27 s (1H, C^4H), 7.37-7.43 m ($3H_{Ph}$), 7.64-7.66 m ($2H_{Ph}$). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 75.5 q (C^2, $J_{C\text{-}F}$ 32.5 Hz), 117.6 q (C^3, $J_{C\text{-}F}$ 1.1 Hz), 123.7 q (C^1, $J_{C\text{-}F}$ 284.0 Hz), 128.4, 129.2, 129.4, 134.2, 134.8 q (C^4, $J_{C\text{-}F}$ 0.5 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: -76.45 d (CF_3, $J_{H\text{-}F}$ 6.1 Hz).



(*Z*)-3-Bromo-1,1,1-trifluoro-4-(3-methylphenyl)but-3-en-2-ol (2b): pale yellow oil. The reaction scale is 200 mg (0.68 mmol) (*Z*)-3-bromo-1,1,1-trifluoro-4-(3-methylphenyl)but-3-en-2-one, isolated amount is 200 mg, 99% yield. ^1H NMR ($CDCl_3$, 400 MHz) δ, ppm: 2.39 s (3H, CH_3), 2.97 d (1H, OH, ^3J 8.5 Hz), 4.66-4.72 m (1H, C^2H), 7.19 d ($1H_{arom.}$, ^3J 7.6 Hz), 7.23 s (1H, C^4H), 7.30 t ($1H_{arom.}$, ^3J 7.6 Hz), 7.44 s ($1H_{arom.}$), 7.47 d ($1H_{arom.}$, ^3J 7.8 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 21.5 (CH_3), 75.5 q (C^2, $J_{C\text{-}F}$ 32.5 Hz), 117.3 q (C^3, $J_{C\text{-}F}$ 1.3 Hz), 123.7 q (C^1, $J_{C\text{-}F}$ 284.0 Hz), 126.4, 128.4, 130.0, 130.1, 134.1, 135.0 q (C^4, $J_{C\text{-}F}$ 0.7 Hz), 138.2. ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: -76.48 d (CF_3, $J_{H\text{-}F}$ 6.1 Hz). HRMS (ESI): $C_{11}H_9BrF_3OAg$ found 400.8921 $[M+Ag]^+$; calcd. 400.8913.

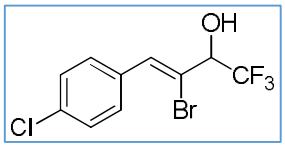


(*Z*)-3-Bromo-1,1,1-trifluoro-4-(4-methylphenyl)but-3-en-2-ol (2c):[5] colorless oil. The reaction scale is 200 mg (0.68 mmol) (*Z*)-3-bromo-1,1,1-trifluoro-4-(4-methylphenyl)but-3-en-2-one, isolated



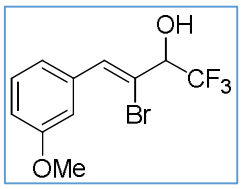
amount is 197 mg, 98% yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 2.37 s (3H, CH_3), 3.02 br. s (1H, OH), 4.68 q (1H, C^2H, $^{3}J_{H\text{-}F}$ 6.1 Hz), 7.21 d ($2H_{arom.}$, ^{3}J 8.1 Hz), 7.22 s (1H, C^4H), 7.57 d ($2H_{arom.}$, ^{3}J 8.1 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 21.5 (CH_3), 75.6 q (C^2, $J_{C\text{-}F}$ 32.5 Hz), 116.5 q (C^3, $J_{C\text{-}F}$ 1.2 Hz), 123.7 q (C^1, $J_{C\text{-}F}$ 284.0 Hz), 129.2, 129.4, 131.3, 134.8 q (C^4, $J_{C\text{-}F}$ 0.5 Hz), 139.5. ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: -76.48 d (CF_3, $J_{H\text{-}F}$ 6.1 Hz).

(*Z*)-3-Bromo-4-(4-chlorophenyl)-1,1,1-trifluorobut-3-en-2-ol (2d):[5] pale yellow oil.



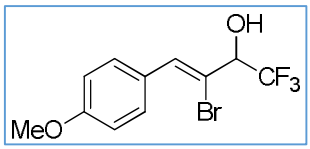
The reaction scale is 200 mg (0.64 mmol) (*Z*)-3-bromo-1,1,1-trifluoro-4-(4-chlorophenyl)but-3-en-2-one, isolated amount is 194 mg, 96% yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 3.02 d (1H, OH, ^{3}J 8.1 Hz), 4.67-4.73 m (1H, C^2H), 7.22 s (1H, C^4H), 7.37 d ($2H_{arom.}$, ^{3}J 8.5 Hz), 7.58 d ($2H_{arom.}$, ^{3}J 8.5 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 75.5 q (C^2, $J_{C\text{-}F}$ 32.5 Hz), 118.3 q (C^3, $J_{C\text{-}F}$ 1.2 Hz), 123.6 q (C^1, $J_{C\text{-}F}$ 283.9 Hz), 128.8, 130.7, 132.6, 133.6 q (C^4, $J_{C\text{-}F}$ 0.5 Hz), 135.11. ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: -76.45 d (CF_3, $J_{H\text{-}F}$ 6.1 Hz).

(*Z*)-3-Bromo-1,1,1-trifluoro-4-(3-methoxyphenyl)but-3-en-2-ol (2e): pale yellow oil.

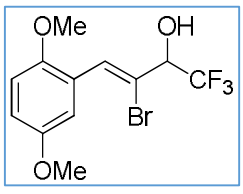


The reaction scale is 220 mg (0.71 mmol) (*Z*)-3-bromo-1,1,1-trifluoro-4-(3-methoxyphenyl)but-3-en-2-one, isolated amount is 217 mg, 98% yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 2.99 d (1H, OH, ^{3}J 8.3 Hz), 3.84 s (3H, CH_3), 4.70 m (1H, C^2H), 6.93 dd ($1H_{arom.}$, ^{3}J 8.2 Hz, ^{4}J 1.9 Hz), 7.19 d ($1H_{arom.}$, ^{3}J 8.0 Hz), 7.24 s (2H, C^4H, $H_{arom.}$), 7.31 t ($1H_{arom.}$, ^{3}J 8.0 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 55.5 (CH_3), 75.5 q (C^2, $J_{C\text{-}F}$ 32.5 Hz), 114.6, 115.0, 117.7 q (C^3, $J_{C\text{-}F}$ 1.1 Hz), 122.1, 123.6 q (C^1, $J_{C\text{-}F}$ 284.1 Hz), 129.5, 134.7 q (C^4, $J_{C\text{-}F}$ 0.5 Hz), 135.4, 159.5. ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: -76.45 d (CF_3, $J_{H\text{-}F}$ 6.1 Hz). HRMS (ESI): $C_{11}H_{10}BrF_3O_2Ag$ found 416.8870 $[M+Ag]^+$; calcd. 416.8862.

(*Z*)-3-Bromo-1,1,1-trifluoro-4-(4-methoxyphenyl)but-3-en-2-ol (2f):[5] colorless oil. The



reaction scale is 200 mg (0.65 mmol) (*Z*)-3-bromo-1,1,1-trifluoro-4-(4-methoxyphenyl)but-3-en-2-one, isolated amount is 140 mg, 69% yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 2.98-3.03 m (1H, OH), 3.84 s (3H, CH_3), 4.64-4.70 m (1H, C^2H), 6.92 d ($2H_{arom.}$, ^{3}J 8.9 Hz), 7.17 s (1H, C^4H), 7.66 d ($2H_{arom.}$, ^{3}J 8.8 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 55.5 (CH_3), 75.7 q (C^2, $J_{C\text{-}F}$ 32.5 Hz), 113.9, 115.1 q (C^3, $J_{C\text{-}F}$ 1.0 Hz), 123.7 q (C^1, $J_{C\text{-}F}$ 284.0 Hz), 126.5, 131.1, 134.2 q (C^4, $J_{C\text{-}F}$ 0.5 Hz), 160.3. ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: -76.49 dd (CF_3, $J_{H\text{-}F}$ 6.0 Hz, $J_{H\text{-}F}$ 3.6 Hz).



(*Z*)-3-Bromo-1,1,1-trifluoro-4-(2,5-dimethoxyphenyl)but-3-en-2-ol (2g): colorless oil. The reaction scale is 100 mg (0.29 mmol) (*Z*)-3-bromo-1,1,1-trifluoro-4-(2,5-dimethylphenyl)but-3-en-2-one, isolated amount is 74 mg, 75% yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 2.96 d

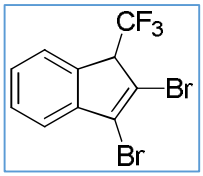
(1H, OH, ^{3}J 7.8 Hz), 3.79 s (3H, CH_3), 3.80 s (3H, CH_3), 4.70-4.74 m (1H, C^2H), 6.83 d (1$H_{arom.}$, ^{3}J 9.0 Hz), 6.90 dd (1$H_{arom.}$, ^{3}J 9.0 Hz, ^{4}J 3.0 Hz), 7.42 s (1H, C^4H), 7.44 d (1$H_{arom.}$, ^{4}J 3.0 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 56.0 (CH_3), 56.3 (CH_3), 75.5 q (C^2, J_{C-F} 32.6 Hz), 111.9, 115.3, 115.8, 118.3 q (C^3, J_{C-F} 1.1 Hz), 123.7 q (C^1, J_{C-F} 284.0 Hz), 123.8, 130.6 q (C^4, J_{C-F} 0.6 Hz), 151.8, 153.1. ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: -76.43 d (CF_3, J_{H-F} 6.2 Hz). HRMS (ESI): $C_{12}H_{12}BrF_3O_3Ag$ found 446.8976 $[M+Ag]^+$; calcd. 446.8967.

General Procedure and Characterization data

General procedure for transformations of compounds *E*-, *Z*-1a-f in superacid TfOH. Synthesis of compounds 3a-e and 4a-e.

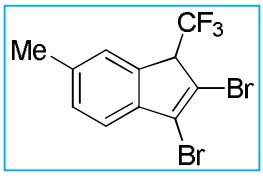
A solution *E*-, *Z*-isomers CF_3-alcohol **1** (0.1 mmol) in CH_2Cl_2 (1 mL) was added to TfOH (0.5 mL) at -35 °C / 20 °C. Reaction mixture was magnetically stirred for 15-60 min. Then the mixture was poured into ice water (30 mL) or dry acetonitrile (20 ml) and extracted with chloroform (2×40 mL). The extracts were combined, washed with water (2×40 ml) and dried over Na_2SO_4. The solvent was distilled off under reduced pressure. The crude mixture was purified by preparative TLC on silica gel, using petroleum ether or petroleum ether-EtOAc mixtures (96:4, 9:1) as an eluent.

2,3-Dibromo-1-(trifluoromethyl)-1*H*-indene (**3a**): Colorless oil. The reaction scale is



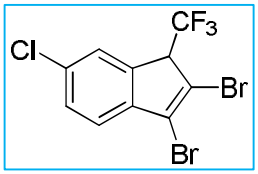
100 mg (0.28 mmol) alcohol **1a** at -35 °C, isolated amount is 26 mg **3a** (yield 27%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 4.22 q (1H, C^1H, $^{3}J_{H-F}$ 8.5 Hz), 7.34 td (1H, $H_{arom.}$, ^{3}J 7.4 Hz, ^{4}J 1.4 Hz), 7.40-7.48 m (2H, $H_{arom.}$), 7.55 d (1H, $H_{arom.}$, ^{3}J 7.4 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 56.8 q (C^1, J_{C-F} 29.8 Hz), 118.8 q (C^2, J_{C-F} 2.4 Hz), 121.1, 124.4 q (CF_3, J_{C-F} 280.6 Hz), 124.7 q (C^7, J_{C-F} 1.5 Hz), 127.6, 129.4 (C^3), 129.6, 135.6 q (J_{C-F} 1.6 Hz), 142.4. ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: -66.52 dd (CF_3, J_{H-F} 8.5 Hz, J_{H-F} 1.4 Hz). HRMS (MALDI-TOF): $C_{10}H_6Br_2F_3$ found 340.8774 $[M+H]^+$; calcd. 340.8783.

2,3-Dibromo-1-(trifluoromethyl)-6-methyl-1*H*-indene (3b): Pale yellow oil. The



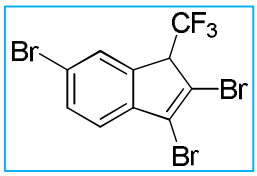
reaction scale is 100 mg (0.27 mmol) alcohol **1b** at -35 °C, isolated amount is 45 mg **3b** (yield 47%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 2.42 s (3H, CH_3), 4.17 q (1H, C^1H, $^{3}J_{H-F}$ 8.6 Hz), 7.24-7.29 m (2H, C^4H, C^5H), 7.35 s (1H, C^7H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 21.7 (CH_3), 56.6 q (C^1, J_{C-F} 29.7 Hz), 117.4 q (C^2, J_{C-F} 2.6 Hz), 120.8, 124.5 q (CF_3, J_{C-F} 280.4 Hz), 125.5 q (C^7, J_{C-F} 1.4 Hz), 129.3 (C^3), 130.2, 135.7 q (J_{C-F} 1.7 Hz), 137.9, 139.8. ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: -66.55 dd (CF_3, J_{H-F} 8.6 Hz, J_{H-F} 1.2 Hz). HRMS (MALDI-TOF): $C_{11}H_8Br_2F_3$ found 354.8941 $[M+H]^+$; calcd. 354.8939.

2,3-Dibromo-6-chloro-1-(trifluoromethyl)-1*H*-indene (**3c**): Pale brown oil. The



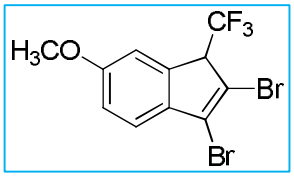
reaction scale is 100 mg (0.25 mmol) alcohol **1c** at 20 °C, isolated amount is 40 mg **3c** (yield 48%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 4.21 q (1H, C^1H, $^{3}J_{H\text{-}F}$ 8.4 Hz), 7.33 d (1H, C^4H, ^{3}J 8.1 Hz), 7.45 dd (1H, C^5H, ^{3}J 8.2 Hz, ^{4}J 1.8 Hz), 7.53 s (1H, C^7H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 56.7 q (C^1, $J_{C\text{-}F}$ 30.2 Hz), 119.1 q (C^2, $J_{C\text{-}F}$ 2.0 Hz), 122.5 q (CF_3, $J_{C\text{-}F}$ 272.2 Hz), 121.9, 125.3 q (C^7, $J_{C\text{-}F}$ 1.6 Hz), 128.6 q ($J_{C\text{-}F}$ 0.7 Hz), 129.9, 134.0 (C^3), 141.0. ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: -66.38 dd (CF_3, $J_{H\text{-}F}$ 8.4 Hz, $J_{H\text{-}F}$ 0.8 Hz). MS (GC-MS, EI), m/z, ($I_{rel.}$, %): 374/376/378 $[M]^+$ (78/100/25), 295/297 (65/24), 275 (8), 260 (27), 240 (18), 225 (16), 217 (14), 201/203 (91/30), 191 (24), 183 (33), 166 (55), 149 (7), 133 (14), 119 (32), 110 (16), 94 (31), 82 (16), 63 (7), 51 (12). HRMS (MALDI-TOF): $C_{10}H_5Br_2ClF_3$ found 374.8391 $[M+H]^+$; calcd. 374.8393.

2,3,6-Tribromo-1-(trifluoromethyl)-1*H*-indene (**3d**): Red-brown oil. The reaction scale



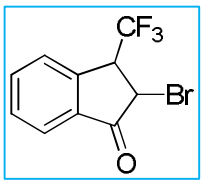
is 100 mg (0.23 mmol) alcohol **1d** at 20 °C, isolated amount is 60 mg **3d** (yield 62%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 4.21 q (1H, C^1H, $^{3}J_{H\text{-}F}$ 8.4 Hz), 7.27 d (1H, C^4H, ^{3}J 8.1 Hz), 7.61 dd (1H, C^5H, ^{3}J 8.1 Hz, ^{4}J 1.6 Hz), 7.68 s (1H, C^7H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 56.7 q (C^1, $J_{C\text{-}F}$ 30.1 Hz), 119.2 q (C^2, $J_{C\text{-}F}$ 2.2 Hz), 121.9, 122.2, 124.1 q (CF_3, $J_{C\text{-}F}$ 280.7 Hz), 128.0 q (C^7, $J_{C\text{-}F}$ 1.7 Hz), 128.7 (C^3), 132.8, 137.1 q ($J_{C\text{-}F}$ 1.7 Hz), 141.4. ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: -66.33 dd (CF_3, $J_{H\text{-}F}$ 8.4 Hz, $J_{H\text{-}F}$ 0.9 Hz). MS (GC-MS, EI), m/z, ($I_{rel.}$, %): 418/420/422/424 $[M]^+$ (16/44/40/15), 398/400/402/404 (3/9/11/4), 339/341/343 (50/100/51), 320/322/324 (3/10/3), 289/291/293 (5/12/7), 260/262 (24/22), 208 (18), 191 (10), 180 (28), 161 (13), 130 (33), 111 (14), 91 (20), 81 (11), 62 (11). HRMS (MALDI-TOF): $C_{10}H_5Br_3F_3$ found 418.7889 $[M+H]^+$; calcd. 418.7888.

2,3-Dibromo-1-(trifluoromethyl)-6-methoxy-1*H*-indene (**3e**): Red-brown solid, mp 77-

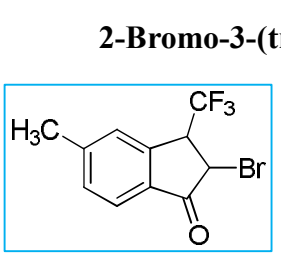


79°C (MeOH). The reaction scale is 100 mg (0.26 mmol) alcohol **1e** at 20 °C, isolated amount is 50 mg **3e** (yield 52%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 3.85 s (3H, CH_3), 4.17 q (1H, C^1H, $^{3}J_{H\text{-}F}$ 8.5 Hz), 6.96 dd (1H, C^5H, ^{3}J 8.4 Hz, ^{4}J 2.3 Hz), 7.12 s (1H, C^7H), 7.29 d (1H, C^4H, ^{3}J 8.4 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 55.9 (CH_3), 56.6 q (C^1, $J_{C\text{-}F}$ 29.6 Hz), 111.9 q (C^7, $J_{C\text{-}F}$ 1.5 Hz), 114.4, 115.5 q (C^2, $J_{C\text{-}F}$ 2.4 Hz), 121.7, 124.4 q (CF_3, $J_{C\text{-}F}$ 280.1 Hz), 128.9, 135.3 (C^3), 137.1 q ($J_{C\text{-}F}$ 1.6 Hz), 159.8. ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: -66.72 dd (CF_3, $J_{H\text{-}F}$ 8.5 Hz, $J_{H\text{-}F}$ 1.0 Hz). MS (GC-MS, EI), m/z, ($I_{rel.}$, %): 370/372/374 $[M]^+$ (31/56/29), 291/293 (96/100), 276/278 (9/8), 248/250 (10/11), 212 (8), 169 (13), 115 (5), 99 (9), 74 (9). HRMS (MALDI-TOF): $C_{11}H_8OBr_2F_3$ found 370.8892 $[M+H]^+$; calcd. 370.8889.

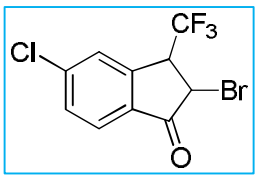
2-Bromo-3-(trifluoromethyl)indan-1-one (**4a**): Yellow liquid. The reaction scale is 60 mg (0.16 mmol) alcohol **1a** at 20 °C, isolated amount is 24 mg **4a** (yield 54%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 4.31 qd (1H, C^3H, ^3J 3.3 Hz, $^3J_{H\text{-}F}$ 8.5 Hz), 4.67 d (1H, C^2H, ^3J 3.3 Hz), 7.62 t (1H, C^6H, ^3J 7.5 Hz), 7.68 d (1H, C^4H, ^3J 7.8 Hz), 7.79 dt (1H, C^5H, ^3J 7.5 Hz, ^3J 1.1 Hz), 7.92 d (1H, C^7H, ^3J 7.7 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 41.9 q (C^2, $J_{C\text{-}F}$ 2.1 Hz), 54.1 q (C^3, $J_{C\text{-}F}$ 29.4 Hz), 125.5 q (CF_3, $J_{C\text{-}F}$ 279.6 Hz), 125.7, 127.0 q (C^4, $J_{C\text{-}F}$ 1.0 Hz), 130.7, 134.4, 136.7, 144.1 q ($J_{C\text{-}F}$ 2.0 Hz), 195.9 (C^1). ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: -69.67 d (CF_3, $J_{H\text{-}F}$ 8.5 Hz). MS (GC-MS, EI), m/z, ($I_{rel.}$, %): 278/280 $[M]^+$ (53/55), 199 (100), 179 (26), 151 (75), 130 (29), 121 (15), 102 (72), 76 (50), 51 (30). HRMS (ESI): $C_{10}H_6OBrF_3Na$ found 300.9449 $[M+Na]^+$; calcd. 300.9446.



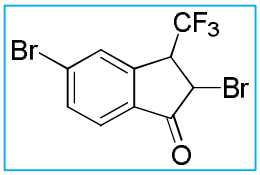
2-Bromo-3-(trifluoromethyl)-5-methylindan-1-one (**4b**): Yellow oil. The reaction scale is 60 mg (0.16 mmol) alcohol **1b** at 20 °C, isolated amount is 24 mg **4b** (yield 54%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 2.52 s (3H, CH_3), 4.25 qd (1H, C^3H, ^3J 3.3 Hz, $^3J_{H\text{-}F}$ 8.5 Hz), 4.65 d (1H, C^2H, ^3J 3.3 Hz), 7.41 d (1H, C^6H, ^3J 7.9 Hz), 7.46 s (1H, C^4H), 7.80 d (1H, C^7H, ^3J 7.9 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 22.5 (CH_3), 42.3 q (C^2, $J_{C\text{-}F}$ 2.1 Hz), 54.0 q (C^3, $J_{C\text{-}F}$ 29.3 Hz), 125.5, 125.5 q (CF_3, $J_{C\text{-}F}$ 279.6 Hz), 127.2 q (C^4, $J_{C\text{-}F}$ 1.0 Hz), 131.9, 132.1, 144.5 q ($J_{C\text{-}F}$ 1.9 Hz), 148.6 (C^5), 195.3 (C^1). ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: -69.51 dd (CF_3, $J_{H\text{-}F}$ 8.5 Hz, $J_{H\text{-}F}$ 0.9 Hz). MS (GC-MS, EI), m/z, ($I_{rel.}$, %): 292/294 $[M]^+$ (25/25), 231 (100), 193 (11), 165 (23), 144 (11), 115 (36), 89 (10), 57 (12). HRMS (ESI): $C_{11}H_8BrF_3NaO$ found 314.9612 $[M+Na]^+$, calcd. 314.9608.



2-Bromo-5-chloro-3-(trifluoromethyl)indan-1-one (4c): Yellow oil. The reaction scale is 60 mg (0.16 mmol) alcohol **1c** at 20 °C, isolated amount is 12 mg **4c** (yield 25%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 4.28 qd (1H, C^3H, ^3J 3.3 Hz, $^3J_{H\text{-}F}$ 8.5 Hz), 4.67 d (1H, C^2H, ^3J 3.3 Hz), 7.60 dd (1H, C^6H, ^3J 8.2 Hz, ^4J 1.1 Hz), 7.67 s (1H, C^4H), 7.86 d (1H, C^7H, ^3J 8.2 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 41.6 q (C^2, $J_{C\text{-}F}$ 2.1 Hz), 53.9 q (C^3, $J_{C\text{-}F}$ 29.7 Hz), 125.2 q (CF_3, $J_{C\text{-}F}$ 279.6 Hz), 126.7, 127.3 q (C^4, $J_{C\text{-}F}$ 1.3 Hz), 131.6, 132.8, 143.6, 145.4 q ($J_{C\text{-}F}$ 2.0 Hz), 194.4 (C^1). ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: -69.57 d (CF_3, $J_{H\text{-}F}$ 8.5 Hz). MS (GC-MS, EI), m/z, ($I_{rel.}$, %): 312/314/316 $[M]^+$ (27/35/9), 233/235 (100/32), 213 (8), 185 (16), 164 (8), 136 (14), 99 (11), 75 (24), 68 (10), 50 (9). HRMS (ESI): $C_{10}H_5BrClF_3NaO$ found 334.9064 $[M+Na]^+$, calcd. 334.9062.

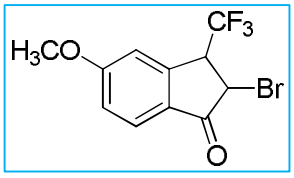


2,5-Dibromo-3-(trifluoromethyl)indan-1-one (4d): Brown oil. The reaction scale is 60 mg (0.14 mmol) alcohol **1d** at 20 °C, isolated amount is 16 mg **4d** (yield 32%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 4.28 qd (1H, C^3H, ^3J 3.3 Hz, $^3J_{H\text{-}F}$ 8.5 Hz), 4.65 d (1H, C^2H, ^3J 3.3



Hz), 7.75-7.79 m (2H, C^6H, C^7H), 7.85 s (1H, C^4H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 41.5 q (C^2, J_{C-F} 2.1 Hz), 53.8 q (C^3, J_{C-F} 29.6 Hz), 125.2 q (CF_3, J_{C-F} 279.7 Hz), 126.7, 130.3 q (C^4, J_{C-F} 1.0 Hz), 132.4, 133.2, 134.5, 145.4 q (J_{C-F} 2.0 Hz), 194.7 (C^1). ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: -69.54 d (CF_3, J_{H-F} 8.5 Hz). MS (GC-MS, EI), m/z, ($I_{rel.}$, %): 356/358/360 $[M]^+$ (27/52/25), 277/279 (100/96), 229/231 (9/9), 198 (27), 170 (16), 151 (10), 120 (11), 101 (20), 75 (34), 50 (16). HRMS (ESI): $C_{10}H_5Br_2F_3NaO$ found 378.8565 $[M+Na]^+$, calcd. 378.8557.

2-Bromo-3-(trifluoromethyl)-5-methoxyindan-1-one (4e): Brown oil. The reaction



scale is 60 mg (0.15 mmol) alcohol **1e** at 20 °C, isolated amount is 15 mg **4e** (yield 33%). ^1H NMR ($CDCl_3$, 400 MHz) δ, ppm: 3.94 s (CH_3), 4.24 qd (1H, C^3H, ^3J 3.3 Hz, $^3J_{H-F}$ 8.6 Hz), 4.65 d (1H, C^2H, ^3J 3.3 Hz), 7.06 s (1H, C^4H), 7.11 dd (1H, C^6H, ^3J 8.6 Hz, ^4J 2.1 Hz), 7.84 d (1H, C^7H, ^3J 8.6 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 42.5 q (C^2, J_{C-F} 2.1 Hz), 54.0 q (C^3, J_{C-F} 29.2 Hz), 56.2 (CH_3), 110.5 q (C^4, J_{C-F} 1.1 Hz), 118.3, 125.5 q (CF_3, J_{C-F} 279.6 Hz), 127.4, 127.5, 146.9 q (J_{C-F} 1.9 Hz), 166.8 (C^5), 193.9 (C^1). ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: -69.57 d (CF_3, J_{H-F} 8.6 Hz). MS (GC-MS, EI), m/z, ($I_{rel.}$, %): 308/310 $[M]^+$ (49/50), 229 (100), 201 (10), 181 (12), 160 (21), 151 (6), 132 (8), 102 (8), 89 (14), 75 (8), 63 (13), 51 (5). HRMS (ESI): $C_{11}H_8BrF_3NaO_2$ found 330.9565 $[M+Na]^+$, calcd. 330.9557.

General procedure for reaction of compounds *E*-, *Z*-1a-f with arenes in superacid TfOH. Synthesis of compounds *E*-, *Z*-5a-m and 6a-d.

An *E*-, *Z*-isomers CF_3-alcohol **1** (0.1 mmol) was added to mixture of TfOH (0.5 mL) with benzene (5 mmol) or another arene (0.11 mmol) in CH_2Cl_2 (1 mL) at 20 °C. Reaction mixture was magnetically stirred for 1 h. Then the mixture was poured into ice water (30 mL) and extracted with chloroform (2×40 mL). The extracts were combined, washed with water, a saturated aqueous solution of $NaHCO_3$, water again, and dried over Na_2SO_4. The solvent was distilled off under reduced pressure. The crude mixture was purified by preparative TLC on silica gel, using petroleum ether or petroleum ether-EtOAc mixtures (9:1) as an eluent.

General procedure for reaction of compounds 3a-e with arenes in superacid TfOH. Synthesis of compounds 6a-h and 7a-m.

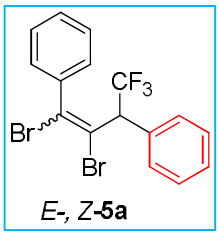
A dibromoindene **3** (0.1 mmol) was added to mixture of TfOH (0.5 mL) with benzene (5 mmol) or another arene (0.11 mmol) in CH_2Cl_2 (1 mL) at 20 °C. Reaction mixture was magnetically stirred for 10 min. Then the mixture was poured into ice water (30 mL) and extracted with chloroform (2×40 mL). The extracts were combined, washed with water, a saturated aqueous solution of $NaHCO_3$, water again, and dried over Na_2SO_4. The solvent was

distilled off under reduced pressure. The crude mixture was purified by preparative TLC on silica gel, using petroleum ether or petroleum ether-EtOAc mixtures (9:1) as an eluent.

General procedure for reaction of compounds 2a-g with arenes in superacid TfOH. Synthesis of compounds 8a-w, 9a-x and 10a,b.

CF_3-alcohol **2** (0.1 mmol) was added to the mixture of TfOH (0.5 mL), CH_2Cl_2 (1 mL) and benzene (0.11 mmol) or another arene (0.11 mmol) at -35 °C. Reaction mixture was magnetically stirred for 1 h, then poured into ice water (30 mL) and extracted with chloroform (2×40 mL). The extracts were combined, washed with water, then with saturated aqueous $NaHCO_3$, with water again, and dried over Na_2SO_4. The solvent was distilled off under reduced pressure. The crude mixture was purified by preparative TLC on silica gel using petroleum ether or petroleum ether-EtOAc mixtures (9:1) as an eluent.

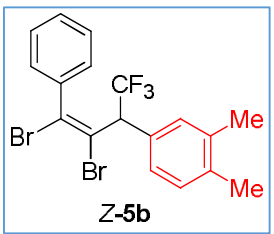
(*E*-) and (*Z*)-3,4-Dibromo-1,1,1-trifluoro-2,4-diphenylbut-3-ene (*E*-, *Z*-5a): The



E-, *Z*-**5a**

reaction scale is 60 mg (0.16 mmol) alcohol **1a** and 654 mg (8.4 mmol) benzene, isolated amount is 50 mg mixture of *E*-, *Z*-isomers **5a** and bromoindene **6a** in ratio *E*-**5a** : *Z*-**5a** : **6a** = 1:2:1.7 (total yield mixture of *E*-, *Z*-isomers **5a** 42%, ratio *E*- : *Z*- = 1:2). *E*-isomer: ^{1}H NMR ($CDCl_3$, 400 MHz, measured in a mixture with *Z*-isomer and **6a**) δ, ppm: ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 5.64 q (1H, C^2H, $^3J_{H\text{-}F}$ 9.0 Hz) 7.19-7.21 m ($1H_{arom.}$), 7.28-7.39 m ($2H_{arom.}$), 7.40-7.49 m ($5H_{arom.}$), 7.56-7.60 m ($2H_{arom.}$). ^{13}C NMR ($CDCl_3$, 100 MHz, measured in a mixture with *Z*-isomer and **6a**) δ, ppm: 56.2 q (C^2, $J_{C\text{-}F}$ 28.9 Hz), 116.2 q (C^3, $J_{C\text{-}F}$ 2.1 Hz), 123.3, 125.3 q (C^1, $J_{C\text{-}F}$ 280.3 Hz), 128.8, 128.9, 128.9, 129.0, 129.2 q ($J_{C\text{-}F}$ 1.2 Hz), 129.3, 130.5, 140.4. ^{19}F NMR ($CDCl_3$, 376 MHz, measured in a mixture with *Z*-isomer and **6a**) δ, ppm: -64.52 d (CF_3, $J_{H\text{-}F}$ 8.9 Hz). MS (GC-MS, EI), m/z, ($I_{rel.}$, %): 418/420/422 (15/35/10) $[M]^+$, 339/341 (20/20), 260 (100), 240 (13), 191 (78), 109 (7), 95 (70), 82 (20). HRMS (MALDI-TOF): $C_{16}H_{12}Br_2F_3$ found 418.9261 $[M+H]^+$; calcd. 418.9253. *Z*-isomer: ^{1}H NMR ($CDCl_3$, 400 MHz, measured in a mixture with *E*-isomer and **6a**) δ, ppm: 4.67 q (1H, C^2H, $^3J_{H\text{-}F}$ 8.8 Hz) 7.28-7.39 m ($8H_{arom.}$), 7.40-7.49 m ($2H_{arom.}$). ^{13}C NMR ($CDCl_3$, 100 MHz, measured in a mixture with *E*-isomer and **6a**) δ, ppm: 54.1 q (C^2, $J_{C\text{-}F}$ 29.0 Hz), 122.2 q (C^3, $J_{C\text{-}F}$ 1.8 Hz), 124.7 q (C^1, $J_{C\text{-}F}$ 282.0 Hz), 125.0, 128.4, 128.4, 128.6, 128.9, 129.3, 129.7, 132.5, 139.2. ^{19}F NMR ($CDCl_3$, 376 MHz, measured in a mixture with *E*-isomer and **6a**) δ, ppm: -64.51 d (CF_3, $J_{H\text{-}F}$ 8.8 Hz). MS (GC-MS, EI), m/z, ($I_{rel.}$, %): 418/420/422 (18/30/15) $[M]^+$, 339/341 (32/32), 260 (100), 191 (63), 165 (10), 130 (5), 109 (19), 95 (51), 82 (23), 51 (8). HRMS (MALDI-TOF): $C_{16}H_{12}Br_2F_3$ found 418.9261 $[M+H]^+$; calcd. 418.9253.

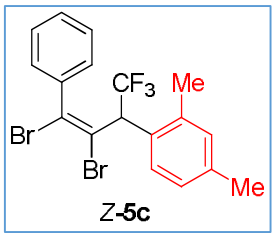
(*Z*)-3,4-Dibromo-1,1,1-trifluoro-2-(3,4-dimethylphenyl)-4-phenylbut-3-ene (*Z*-5b): Colorless solid, mp 77-79°C (MeOH). The



Z-**5b**

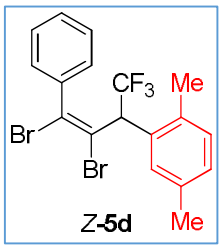
reaction scale is 60 mg (0.16 mmol) alcohol **1a** and 20 mg (0.18 mmol) *ortho*-xylene, isolated amount is 60 mg *Z*-**5a** (yield 84%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 2.25 s (3H, CH_3), 2.26 s (3H, CH_3), 4.60 q (1H, C^2H, $^{3}J_{H\text{-}F}$ 8.9 Hz) 7.05 d (1H, $H_{arom.}$), 7.06 s (1H, $H_{arom.}$), 7.11 d (1$H_{arom.}$, ^{3}J 8.5 Hz), 7.33-7.35 m (2$H_{arom.}$), 7.42-7.48 (3H, $H_{arom.}$). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 19.6 (CH_3), 20.1 (CH_3), 53.7 q (C^2, $J_{C\text{-}F}$ 29.0 Hz), 122.6 q (C^3, $J_{C\text{-}F}$ 1.7 Hz), 124.8 q (C^1, $J_{C\text{-}F}$ 282.0 Hz), 126.4 q ($J_{C\text{-}F}$ 0.9 Hz), 128.5, 129.2, 129.6, 129.8 (C^4), 130.1, 130.1, 130.2 q ($J_{C\text{-}F}$ 1.0 Hz), 137.1, 137.4, 139.2. ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: -64.62 d (CF_3, $J_{H\text{-}F}$ 8.9 Hz). MS (GC-MS, EI), m/z, ($I_{rel.}$, %): 446/448/450 $[M]^+$ (5/12/5), 367/369 (78/80), 288 (100), 273 (33), 253 (5), 219 (50), 189 (5), 137 (8), 115 (7), 101 (19), 77 (9), 63 (5). HRMS (MALDI-TOF): $C_{18}H_{16}Br_2F_3$ found 446.9565 $[M+H]^+$; calcd. 446.9565.

(*Z*)-3,4-Dibromo-1,1,1-trifluoro-2-(2,4-dimethylphenyl)-4-phenylbut-3-ene (*Z*-5c):



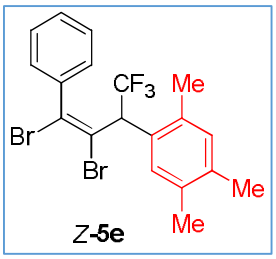
Colorless solid, mp 80-83°C (MeOH). The reaction scale is 60 mg (0.16 mmol) alcohol **1a** and 20 mg (0.18 mmol) *meta*-xylene, isolated amount is 54 mg *Z*-**5c** (yield 77%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 1.56 s (3H, CH_3), 2.29 s (3H, CH_3), 4.93 q (1H, C^2H, $^{3}J_{H\text{-}F}$ 8.9 Hz), 6.88 s (1$H_{arom.}$), 7.05 d (1$H_{arom.}$, ^{3}J 8.1 Hz), 7.28-7.30 m (2$H_{arom.}$), 7.40-7.42 m (3$H_{arom.}$), 7.84 d (1$H_{arom.}$, ^{3}J 8.1 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 19.2 (CH_3), 21.1 (CH_3), 49.0 q (C^2, $J_{C\text{-}F}$ 28.9 Hz), 122.0 q (C^3, $J_{C\text{-}F}$ 1.8 Hz), 125.1 q (C^1, $J_{C\text{-}F}$ 282.0 Hz), 127.0, 128.2, 128.7, 129.1, 129.2 q ($J_{C\text{-}F}$ 1.3 Hz), 129.6, 130.6 (C^4), 131.7, 136.9, 138.6, 139.2. ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: -64.79 d (CF_3, $J_{H\text{-}F}$ 8.9 Hz). MS (GC-MS, EI), m/z, ($I_{rel.}$, %): 446/448/450 $[M]^+$ (10/23/10), 367/369 (85/80), 299 (5), 288 (100), 268 (16), 219 (35), 189 (5), 171 (5), 134 (6), 115 (6), 101 (15), 77 (7), 51 (5). HRMS (MALDI-TOF): $C_{18}H_{16}Br_2F_3$ found 446.9567 $[M+H]^+$; calcd. 446.9565.

(*Z*)-3,4-Dibromo-1,1,1-trifluoro-2-(2,5-dimethylphenyl)-4-phenylbut-3-ene (*Z*-5d):



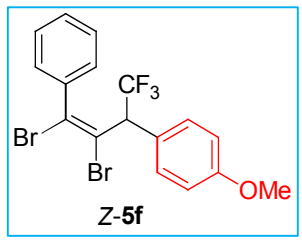
Colorless solid, mp 86-88°C (MeOH). The reaction scale is 60 mg (0.16 mmol) alcohol **1a** and 20 mg (0.18 mmol) *para*-xylene, isolated amount is 54 mg *Z*-**5d** (yield 77%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 1.53 s (3H, CH_3), 2.35 s (3H, CH_3), 4.93 q (1H, C^2H, $^{3}J_{H\text{-}F}$ 8.9 Hz), 6.94 d (1$H_{arom.}$, ^{3}J 7.8 Hz), 7.04 d (1$H_{arom.}$, ^{3}J 7.8 Hz), 7.26-7.28 m (2$H_{arom.}$), 7.39-7.41 m (3$H_{arom.}$), 7.75 s (1$H_{arom.}$). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 18.8 (CH_3), 21.4 (CH_3), 49.1 (C^2), 121.7 q (C^3, $J_{C\text{-}F}$ 1.8 Hz), 125.0 q (C^1, $J_{C\text{-}F}$ 282.0 Hz), 128.7, 129.1, 129.5, 129.6, 129.8 q ($J_{C\text{-}F}$ 1.2 Hz), 130.7 (C^4), 130.7, 131.0 q ($J_{C\text{-}F}$ 0.5 Hz), 133.9, 135.8, 139.2. ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: -64.80 d (CF_3, $J_{H\text{-}F}$ 8.9 Hz). MS (GC-MS, EI), m/z, ($I_{rel.}$, %): 446/448/450 (2/6/2) $[M]^+$, 367/369 (95), 288 (100), 273 (45), 268 (20), 219 (32), 189 (5), 171 (7), 133 (5), 109 (7), 101 (20), 77 (7), 51 (5). HRMS (MALDI-TOF): $C_{18}H_{16}Br_2F_3$ found 446.9568 $[M+H]^+$; calcd. 446.9565.

(*Z*)-3,4-Dibromo-1,1,1-trifluoro-2-(2,4,5-trimethylphenyl)-4-phenylbut-3-ene (***Z*-5e**): Colorless solid, mp 112-114°C (MeOH). The reaction scale is 60 mg (0.16 mmol) alcohol **1a** and 22 mg (0.18 mmol) pseudocumene, isolated amount is 64 mg *Z*-**5e** (yield 87%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 1.52 s (3H, CH_3), 2.20 s (3H, CH_3), 2.27 s (3H, CH_3), 4.92 q (1H, C^2H, $^{3}J_{H\text{-}F}$ 8.9 Hz), 6.84 s (1H$_{arom.}$), 7.28-7.30 m (2H$_{arom.}$), 7.39-7.42 m (3H$_{arom.}$), 7.72 s (1H$_{arom.}$). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 18.6 (CH_3), 19.5 (CH_3), 19.8 (CH_3), 48.9 q (C^2, $J_{C\text{-}F}$ 28.9 Hz), 122.0 q (C^3, $J_{C\text{-}F}$ 1.7 Hz), 125.1 q (C^1, $J_{C\text{-}F}$ 282.0 Hz), 128.4, 128.7, 129.1, 129.6, 130.2 q ($J_{C\text{-}F}$ 1.1 Hz), 130.5 (C^4), 132.2, 134.2, 134.4, 137.3, 139.2. ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: -64.90 d (CF_3, $J_{H\text{-}F}$ 8.9 Hz). MS (GC-MS, EI), m/z, ($I_{rel.}$, %): 460/462/464 (3) $[M]^+$, 381/383 (100), 302 (100), 286 (60), 233 (25), 217 (10), 203 (13), 169 (5), 141 (6), 115 (7), 91 (20), 77 (7), 51 (5). HRMS (MALDI-TOF): $C_{19}H_{18}Br_2F_3$ found 460.9721 $[M+H]^+$; calcd. 460.9722.



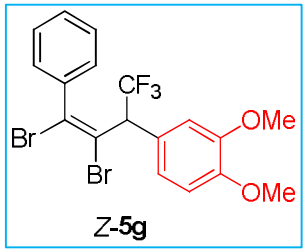
Z-**5e**

(*Z*)-3,4-Dibromo-1,1,1-trifluoro-2-(4-methoxyphenyl)-4-phenylbut-3-ene (***Z*-5f**): The reaction scale is 60 mg (0.16 mmol) alcohol **1a** and 20 mg (0.18 mmol) anisole, isolated amount is 56 mg a mixture of Z-**5f** and **6b** in ratio *Z*-**5f** : **6b** = 4 : 1 (yield *Z*-**5f** 30%). ^{1}H NMR ($CDCl_3$, 400 MHz, measured in a mixture with **6b**) δ, ppm: 3.81 s (3H, CH_3), 4.61 q (1H, C^2H, $^{3}J_{H\text{-}F}$ 8.9 Hz), 6.88 d (2H$_{arom.}$, ^{3}J 8.8 Hz), 7.23 d (2H$_{arom.}$, ^{3}J 8.8 Hz), 7.32-7.36 m (2H$_{arom.}$), 7.42-7.52 m (3H$_{arom.}$). ^{13}C NMR ($CDCl_3$, 100 MHz, measured in a mixture with **6b**) δ, ppm: 53.3 q (C^2, $J_{C\text{-}F}$ 29.2 Hz), 55.3 (CH_3), 114.1, 122.5 q (C^3, $J_{C\text{-}F}$ 1.6 Hz), 124.3, 124.6 q (C^1, $J_{C\text{-}F}$ 282.0 Hz), 126.0, 128.3, 129.1, 130.2 q ($J_{C\text{-}F}$ 1.1 Hz), 130.3, 139.1, 159.7. ^{19}F NMR ($CDCl_3$, 376 MHz, measured in a mixture with **6b**) δ, ppm: -64.93 d (CF_3, $J_{H\text{-}F}$ 8.9 Hz). HRMS (MALDI-TOF): $C_{17}H_{14}Br_2F_3O$ found 448.9342 $[M+H]^+$; calcd. 448.9358.



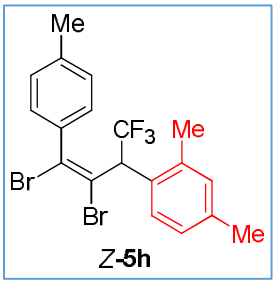
Z-**5f**

(*Z*)-3,4-Dibromo-1,1,1-trifluoro-2-(2,4-dimethoxyphenyl)-4-phenylbut-3-ene (***Z*-5g**): Pale yellow oil. The reaction scale is 60 mg (0.16 mmol) alcohol **1a** and 24 mg (0.18 mmol) veratrole, isolated amount is 10 mg *Z*-**5g** and 26 mg a mixture of *Z*-**5g** and **6c** in ratio *Z*-**5g** : **6c** = 1.2 : 1 (total yield *Z*-**5g** 26%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 3.86 s (3H, CH_3), 3.88 s (3H, CH_3), 4.59 q (1H, C^2H, $^{3}J_{H\text{-}F}$ 8.9 Hz), 6.82-6.85 m (3H$_{arom.}$), 7.32-7.34 m (2H$_{arom.}$), 7.43-7.48 m (3H$_{arom.}$). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 53.6 q (C^2, $J_{C\text{-}F}$ 29.1 Hz), 56.0 (CH_3), 56.0 (CH_3), 111.2, 112.3 q ($J_{C\text{-}F}$ 1.4 Hz), 121.8 q ($J_{C\text{-}F}$ 1.2 Hz), 122.4 q (C^3, $J_{C\text{-}F}$ 1.6 Hz), 124.7 q ($J_{C\text{-}F}$ 1.0 Hz), 124.7 q (C^1, $J_{C\text{-}F}$ 281.9 Hz), 128.4, 129.2, 129.7, 130.0 q ($J_{C\text{-}F}$ 0.9 Hz), 139.5, 149.0, 149.5. ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: -64.93 d (CF_3, $J_{H\text{-}F}$ 8.9 Hz). HRMS (MALDI-TOF): $C_{18}H_{16}Br_2F_3O_2$ found 478.9472 $[M+H]^+$; calcd. 478.9464.



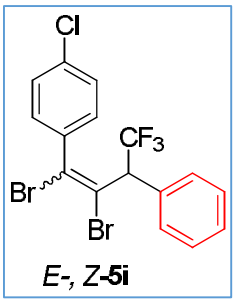
Z-**5g**

(*Z*)-3,4-Dibromo-1,1,1-trifluoro-2-(2,4-dimethylphenyl)-4-(4-methylphenyl)but-3-ene (*Z*-5h): Pale yellow oil. The reaction scale is 60 mg (0.16 mmol) alcohol **1b** and 20 mg (0.18 mmol) *meta*-xylene, isolated amount is 40 mg *Z*-**5h** (yield 54%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 1.61 s (3H, CH_3), 2.29 s (3H, CH_3), 2.40 s (3H, CH_3), 4.95 q (1H, C^2H, $^{3}J_{H\text{-}F}$ 8.9 Hz), 6.89 s ($1H_{arom.}$), 7.05 d ($1H_{arom.}$, ^{3}J 8.6 Hz), 7.18-7.23 m ($4H_{arom.}$), 7.83 d ($1H_{arom.}$, ^{3}J 8.1 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 19.3 (CH_3), 21.1 (CH_3), 21.5 (CH_3), 49.0 q (C^2, $J_{C\text{-}F}$ 29.0 Hz), 121.7 q (C^3, $J_{C\text{-}F}$ 1.7 Hz), 125.1 q (C^1, $J_{C\text{-}F}$ 282.0 Hz), 127.0, 128.3 (C^4), 128.7, 129.2 q ($J_{C\text{-}F}$ 1.4 Hz), 129.7, 130.9, 131.7, 136.3, 137.0, 138.5, 139.8. ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: -64.79 d (CF_3, $J_{H\text{-}F}$ 8.9 Hz). MS (GC-MS, EI), m/z, ($I_{rel.}$, %): 460/462/464 (7/13/5) $[M]^+$, 381/383 (52/49), 302 (100), 287 (46), 283 (11), 233 (37), 217 (10), 202 (13), 151 (8), 115 (21), 108 (16), 101 (10), 95 (7), 77 (9), 65 (5). HRMS (MALDI-TOF): $C_{19}H_{18}Br_2F_3$ found 460.9722 $[M+H]^+$; calcd. 460.9722.



Z-**5h**

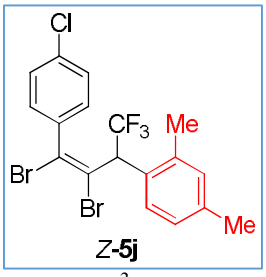
(*E*)- and (*Z*)-3,4-Dibromo-4-(4-chlorophenyl)-1,1,1-trifluoro-2-phenylbut-3-ene (*E*-, *Z*-5i): Yellow solid, mp 77-80°C (MeOH). The reaction scale is 60 mg (0.16 mmol) alcohol **1c** and 592 mg (7.6 mmol) benzene, isolated amount is 42 mg mixture of *E*-, *Z*-isomers **5i** (total yield 58%, ratio *E*- : *Z*- = 1:1.5). *E*-isomer: ^{1}H NMR ($CDCl_3$, 400 MHz, measured in a mixture with *Z*-isomer) δ, ppm: 5.61 q (1H, C^2H, $^{3}J_{H\text{-}F}$ 8.9 Hz), 7.27-7.32 m ($2H_{arom.}$), 7.35-7.38 m ($2H_{arom.}$), 7.42-7.44 m ($3H_{arom.}$), 7.56-7.57 m ($2H_{arom.}$). ^{13}C NMR ($CDCl_3$, 100 MHz, measured in a mixture with *Z*-isomer) δ, ppm: 56.3 q (C^2, $J_{C\text{-}F}$ 29.2 Hz), 117.0 q (C^3, $J_{C\text{-}F}$ 1.6 Hz), 121.9 (C^4), 124.4 q (C^1, $J_{C\text{-}F}$ 281.1 Hz), 129.0, 129.2 q ($J_{C\text{-}F}$ 1.0 Hz), 129.6 (3C), 130.4, 132.3, 135.3, 138.7. ^{19}F NMR ($CDCl_3$, 376 MHz, measured in a mixture with *Z*-isomer) δ, ppm: -64.53 d (CF_3, $J_{H\text{-}F}$ 9.0 Hz). MS (GC-MS, EI), m/z, ($I_{rel.}$, %): 452/454/456/458 (15/33/22/4) $[M]^+$, 373/375/377 (23/30/8), 294/296 (100/34), 274 (16), 259 (40), 225/227 (43/15), 189 (26), 137 (10), 112 (20), 109 (13), 94 (43), 81 (8), 51 (5). HRMS (MALDI-TOF): $C_{16}H_{11}Br_2ClF_3$ found 452.8860 $[M+H]^+$; calcd. 452.8863. *Z*-isomer: ^{1}H NMR ($CDCl_3$, 400 MHz, measured in a mixture with *E*-isomer) δ, ppm: 4.62 q (1H, C^2H, $^{3}J_{H\text{-}F}$ 8.7 Hz), 7.27-7.32 m ($4H_{arom.}$), 7.36 d ($2H_{arom.}$, ^{3}J 8.6 Hz), 7.35-7.38 m ($1H_{arom.}$), 7.45 d ($2H_{arom.}$, ^{3}J 8.7 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz, measured in a mixture with *E*-isomer) δ, ppm: 54.2 q (C^2, $J_{C\text{-}F}$ 29.1 Hz), 122.9 q (C^3, $J_{C\text{-}F}$ 1.9 Hz), 124.6 q (C^1, $J_{C\text{-}F}$ 281.1 Hz), 128.95 (4C), 128.98 (3C), 129.0 (C^4), 129.8, 132.3, 135.9, 137.5. ^{19}F NMR ($CDCl_3$, 376 MHz, measured in a mixture with *E*-isomer) δ, ppm: -64.51 d (CF_3, $J_{H\text{-}F}$ 8.8 Hz). MS (GC-MS, EI), m/z, ($I_{rel.}$, %): 452/454/456/458 (13/29/20/4) $[M]^+$, 373/375/377 (25/33/9), 294/296 (100/32), 274 (16), 259 (41), 239 (7), 225/227 (39/13), 189 (28),



E-, *Z*-**5i**

137 (9), 109 (18), 94 (38), 81 (8), 51 (7). HRMS (MALDI-TOF): $C_{16}H_{11}Br_2ClF_3$ found 452.8860 $[M+H]^+$; calcd. 452.8863.

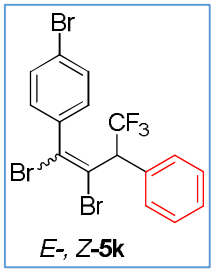
(*Z*)-3,4-Dibromo-4-(4-chlorophenyl)-1,1,1-trifluoro-2-(2,4-dimethylphenyl)but-3-ene



Z-**5j**

(*Z*-5j): Colorless solid, mp 55-57°C (MeOH). The reaction scale is 60 mg (0.16 mmol) alcohol **1c** and 20 mg (0.18 mmol) *meta*-xylene, isolated amount is 54 mg *Z*-**5j** (yield 70%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 1.66 s (3H, CH_3), 2.30 s (3H, CH_3), 4.85 q (1H, C^2H, $^3J_{H\text{-}F}$ 8.8 Hz), 6.92 s ($1H_{arom.}$), 7.06 d ($1H_{arom.}$, ^3J 9.2 Hz), 7.24 d ($2H_{arom.}$, ^3J 8.4 Hz), 7.40 d ($2H_{arom.}$, ^3J 8.6 Hz), 7.80 d ($1H_{arom.}$, ^3J 8.1 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 19.4 (CH_3), 21.1 (CH_3), 49.2 q (C^2, $J_{C\text{-}F}$ 28.9 Hz), 122.7 q (C^3, $J_{C\text{-}F}$ 1.6 Hz), 125.0 q (C^1, $J_{C\text{-}F}$ 282.0 Hz), 127.1, 128.1 (C^4), 129.1 q ($J_{C\text{-}F}$ 0.8 Hz), 129.3, 130.2, 131.7, 135.8, 136.7, 137.6, 138.8. ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: -64.70 d (CF_3, $J_{H\text{-}F}$ 8.8 Hz). MS (GC-MS, EI), m/z, ($I_{rel.}$, %): 480/482/484 (5/10/8) $[M]^+$, 401/403/405 (51/70/17), 322/324 (100/32), 307 (13), 287 (38), 272 (6), 253/255 (42/13), 217 (14), 202 (31), 147 (8), 115 (12), 108 (26), 101 (30), 95 (20), 77 (14), 63 (9), 51 (9). HRMS (MALDI-TOF): $C_{18}H_{15}Br_2ClF_3$ found 480.9179 $[M+H]^+$; calcd. 480.9176.

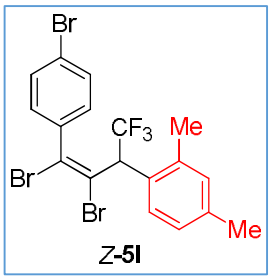
(*E*)- and (*Z*)-3,4-Dibromo-4-(4-bromophenyl)-1,1,1-trifluoro-2-phenylbut-3-ene (*E*-, *Z*-5k): Colorless solid, mp 80-82°C (MeOH). The reaction scale is 60 mg (0.14 mmol) alcohol **1d** and 538 mg (6.9 mmol) benzene, isolated amount is 50 mg mixture of *E*-, *Z*-isomers **5k** (total yield 72%, ratio *E*- : *Z*- = 1:1.8). *E*-isomer: ^{1}H NMR ($CDCl_3$, 400 MHz, measured in a mixture with *Z*-isomer) δ, ppm: 5.60 q (1H, C^2H, $^3J_{H\text{-}F}$ 8.9 Hz), 7.20-7.23 m ($2H_{arom.}$), 7.35-7.38 m ($2H_{arom.}$), 7.42-7.43 m ($1H_{arom.}$), 7.52 d ($2H_{arom.}$, ^3J 8.5 Hz), 7.56-7.58 m ($2H_{arom.}$). ^{13}C NMR ($CDCl_3$, 100 MHz, measured in a mixture with *Z*-isomer) δ, ppm: 56.2 q (C^2, $J_{C\text{-}F}$ 29.2 Hz), 117.0 q (C^3, $J_{C\text{-}F}$ 1.6 Hz), 121.9, 123.6 (C^4), 124.9 q (C^1, $J_{C\text{-}F}$ 282.0 Hz), 128.96, 128.98, 129.2 q ($J_{C\text{-}F}$ 1.2 Hz), 130.6, 131.9, 132.2, 139.2. ^{19}F NMR ($CDCl_3$, 376 MHz, measured in a mixture with *Z*-isomer) δ, ppm: -64.54 d (CF_3, $J_{H\text{-}F}$ 9.1 Hz). MS (GC-MS, EI), m/z, ($I_{rel.}$, %): 496/498/500/502 (10/26/25/9) $[M]^+$, 417/419/421 (9/18/9), 338/340 (91/89), 269/271 (37/37), 259 (100), 239 (9), 189 (43), 135 (20), 119 (23), 109 (17), 95 (49), 81 (13), 51 (7). HRMS (MALDI-TOF): $C_{16}H_{11}Br_3F_3$ found 496.8360 $[M+H]^+$; calcd. 496.8357. *Z*-isomer: ^{1}H NMR ($CDCl_3$, 400 MHz, measured in a mixture with *E*-isomer) δ, ppm: 4.62 q (1H, C^2H, $^3J_{H\text{-}F}$ 8.7 Hz), 7.21 d ($2H_{arom.}$, ^3J 8.4 Hz), 7.31-7.32 m ($2H_{arom.}$), 7.35-7.38 m ($2H_{arom.}$), 7.42-7.43 m ($1H_{arom.}$), 7.61 d ($2H_{arom.}$, ^3J 8.5 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz, measured in a mixture with *E*-isomer) δ, ppm: 54.2 q (C^2, $J_{C\text{-}F}$ 28.9 Hz), 122.9 q (C^3, $J_{C\text{-}F}$ 1.9 Hz), 124.1, 124.6 q (C^1, $J_{C\text{-}F}$ 282.0 Hz), 128.96 (3C), 128.98, 129.0 (C^4), 130.1, 132.2, 132.6, 138.0. ^{19}F NMR ($CDCl_3$, 376 MHz, measured in a mixture with *E*-isomer) δ, ppm: -64.51 d (CF_3, $J_{H\text{-}F}$ 8.9 Hz).MS (GC-MS, EI), m/z,



E-, *Z*-**5k**

($I_{rel.}$, %): 496/498/500/502 (8/23/21/7) $[M]^+$, 417/419/421 (10/21/10), 338/340 (86/82), 269/270 (30/28), 259 (100), 239 (9), 189 (39), 135 (11), 119 (22), 109 (19), 95 (57), 81 (10), 51 (8). HRMS (MALDI-TOF): $C_{16}H_{11}Br_3F_3$ found 496.8360 $[M+H]^+$; calcd. 496.8357.

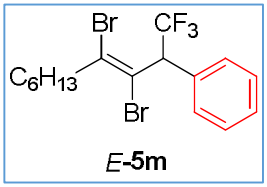
(*Z*)-3,4-Dibromo-4-(4-bromophenyl)-1,1,1-trifluoro-2-(2,4-dimethylphenyl)but-3-ene (*Z*-5l):



Z-5l

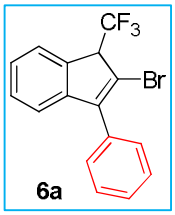
Colorless solid, mp 59-61°C (MeOH). The reaction scale is 60 mg (0.14 mmol) alcohol **1d** and 16 mg (0.16 mmol) *meta*-xylene, isolated amount is 58 mg *Z*-**5l** (yield 79%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 1.66 s (3H, CH_3), 2.30 s (3H, CH_3), 4.84 q (1H, C^2H, $^3J_{H-F}$ 8.7 Hz), 6.91 s ($1H_{arom.}$), 7.06 d ($1H_{arom.}$, ^3J 8.5 Hz), 7.17 d ($2H_{arom.}$, ^3J 8.2 Hz), 7.55 d ($2H_{arom.}$, ^3J 8.5 Hz), 7.79 d ($1H_{arom.}$, ^3J 8.1 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 19.5 (CH_3), 21.1 (CH_3), 49.3 q (C^2, J_{C-F} 28.8 Hz), 122.7 q (C^3, J_{C-F} 1.5 Hz), 124.0, 125.0 q (C^1, J_{C-F} 282.1 Hz), 127.1, 128.1 (C^4), 129.1 q (J_{C-F} 1.3 Hz), 130.4, 131.7, 132.3, 136.7, 138.0, 138.8. ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: -64.70 dd (CF_3, J_{H-F} 8.7 Hz, J_{H-F} 1.8 Hz). MS (GC-MS, EI), m/z, ($I_{rel.}$, %): 524/526/528/530 (4/15/15/4) $[M]^+$, 445/447/449 (33/62/31), 366/368 (87/80), 297/299 (21/20), 287 (100), 272 (10), 218 (13), 202 (20), 133 (9), 108 (24), 101 (17), 95 (15), 77 (6). HRMS (MALDI-TOF): $C_{18}H_{15}Br_3F_3$ found 524.8672 $[M+H]^+$; calcd. 524.8670.

(*E*)-3,4-Dibromo-1,1,1-trifluoro-2-phenyldec-3-ene (*E*-5m): Colorless liquid. The reaction scale is 60 mg (0.16 mmol) alcohol **1f** and 624 mg (8.0 mmol) benzene, isolated amount is 32 mg *E*-**5m** (yield 46%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 0.88 t (3H, CH_3, ^3J 6.8 Hz), 1.28-1.34 m (6H, CH_2), 1.60-1.64 m (2H, CH_2), 2.71-2.85 m (2H, CH_2), 5.50 q (1H, C^2H, $^3J_{H-F}$ 9.1 Hz), 7.36-7.40 m ($3H_{arom.}$), 7.47-7.49 m ($2H_{arom.}$). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 14.1 (CH_3), 22.6 (CH_2), 27.4 (CH_2), 28.2 (CH_2), 31.6 (CH_2), 41.3 (CH_2), 56.0 q (C^2, J_{C-F} 28.8 Hz), 114.3 q (C^3, J_{C-F} 2.0 Hz), 125.1 q (C^1, J_{C-F} 282.1 Hz), 128.6, 128.8, 129.0 q (J_{C-F} 1.2 Hz), 129.1 (C^4), 132.7. ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: -64.57 d (CF_3, J_{H-F} 9.1 Hz). MS (GC-MS, EI), m/z, ($I_{rel.}$, %): 426/428/430 (9/19/8) $[M]^+$, 347/349 (23/24), 263/265/267 (19/20/6), 225 (12), 211 (20), 197 (23), 177 (20), 141 (12), 128 (29), 115 (15), 109 (25), 91 (33), 69 (63), 55 (24), 43 (100). HRMS (MALDI-TOF): $C_{16}H_{20}Br_2F_3$ found 426.9877 $[M+H]^+$; calcd. 426.9878.



E-5m

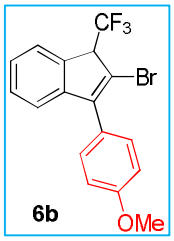
2-Bromo-1-(trifluoromethyl)-3-phenyl-1*H*-indene (6a): Isolated from the reaction of alcohol **1a** (60 mg, 0.16 mmol) and benzene (312 mg, 4.0 mmol), yield 41% (50 mg, mixture of *E*- and *Z*-**5a,** bromoindene **6a** 1:2:1.7, respectively) or from the reaction of dibromoindene **3a** (30 mg, 0.08 mmol) and benzene (654 mg, 8.4 mmol), yield 56% (8 mg mixture of bromoindene **6a** and indene **7a** 8:1, respectively). ^{1}H NMR ($CDCl_3$, 400 MHz, measured in a mixture with **7a**) δ, ppm: 4.34 q (1H, C^1H, $^3J_{H-F}$ 8.7 Hz), 7.24-7.26 m ($1H_{arom.}$), 7.28-7.37 m ($2H_{arom.}$), 7.46-7.49 m ($1H_{arom.}$), 7.51-7.52



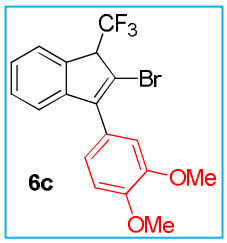
6a

m ($4H_{arom.}$), 7.61-7.62 m ($1H_{arom.}$). ^{13}C NMR ($CDCl_3$, 100 MHz, measured in a mixture with **7a**) δ, ppm: 57.0 q (C^1, J_{C-F} 29.0 Hz), 115.7 q (C^2, J_{C-F} 2.4 Hz), 120.8, 122.6 q (CF_3, J_{C-F} 252.7 Hz), 125.0 q (C^7, J_{C-F} 1.5 Hz), 126.6, 128.8, 128.9, 129.0 129.1, 132.7 (C^3), 137.1 q (J_{C-F} 1.7 Hz), 144.2, 147.8. ^{19}F NMR ($CDCl_3$, 376 MHz, measured in a mixture with **7a**) δ, ppm: -66.28 dd (CF_3, J_{H-F} 8.7 Hz, J_{H-F} 1.0 Hz). MS (GC-MS, EI), m/z, ($I_{rel.}$, %): 338/340 $[M]^+$ (30/30), 259 (100), 239 (13), 209 (7), 189 (20), 119 (15), 94 (25), 81 (5). HRMS (MALDI-TOF): $C_{16}H_{11}BrF_3$ found 338.9980 $[M+H]^+$; calcd. 338.9991.

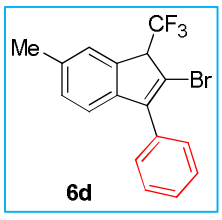
2-Bromo-1-(trifluoromethyl)-3-(4-methoxyphenyl)-1*H*-indene (6b): The reaction scale is 60 mg (0.16 mmol) alcohol **1a** and 20 mg (0.18 mmol) anisole, isolated amount is 56 mg a mixture of *Z*-**5f** and **6b,** ratio *Z*-**5f** : **6b** = 4 : 1 (yield of **6b** 57%). ^1H NMR ($CDCl_3$, 400 MHz, measured in a mixture with *Z*-**5f**) δ, ppm: 3.89 s (3H, CH_3), 4.32 q (1H, C^1H, $^3J_{H-F}$ 8.7 Hz), 7.04 d ($2H_{arom.}$, ^3J 8.8 Hz), 7.28-7.36 m ($2H_{arom.}$), 7.40-7.52 m ($3H_{arom.}$), 7.60 d ($1H_{arom.}$, ^3J 7.3 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz, measured in a mixture with *Z*-**5f**) δ, ppm: 55.3 (CH_3), 56.7 q (C^1, J_{C-F} 28.8 Hz), 114.1, 114.8 q (C^2, J_{C-F} 2.2 Hz), 120.7, 124.8 q (C^7, J_{C-F} 1.3 Hz), 125.1 q (CF_3, J_{C-F} 280.4 Hz), 126.3, 128.8, 129.5, 129.9, 137.0, 144.2, 147.2, 160.0. ^{19}F NMR ($CDCl_3$, 376 MHz, measured in a mixture with *Z*-**5f**) δ, ppm: -66.31 d (CF_3, J_{H-F} 8.7 Hz). HRMS (MALDI-TOF): $C_{17}H_{13}BrF_3O$ found 369.0092 $[M+H]^+$; calcd. 369.0097.



2-Bromo-1-(trifluoromethyl)-3-(3,4-dimethoxyphenyl)-1*H*-indene (6c): Isolated from the reaction of alcohol **1a** (60 mg, 0.16 mmol) and veratrole (24 mg, 0.18 mmol), yield 26% (26 mg, mixture of *Z*-**5g** and bromoindene **6c** 1.2:1, respectively) or from the reaction of dibromoindene **3a** (30 mg, 0.08 mmol) and veratrole (14 mg, 0.10 mmol), yield 44% (16 mg mixture of bromoindene **6c** and indene **7e** 11.5:1, respectively). ^1H NMR ($CDCl_3$, 400 MHz, measured in a mixture with **7c**) δ, ppm: 3.93 s (3H, CH_3), 3.96 s (3H, CH_3), 4.33 q (1H, C^1H, $^3J_{H-F}$ 8.9 Hz), 7.01 d ($1H_{arom.}$, ^3J 8.3 Hz), 7.05 d ($1H_{arom.}$, ^4J 2.0 Hz), 7.10 dd ($1H_{arom.}$, ^3J 7.3 Hz, ^4J 2.0 Hz), 7.28-7.39 m ($3H_{arom.}$), 7.60-7.62 m ($1H_{arom.}$). ^{13}C NMR ($CDCl_3$, 100 MHz, measured in a mixture with **7c**) δ, ppm: 56.1 (CH_3), 56.2 (CH_3), 56.9 q (C^1, J_{C-F} 28.9 Hz), 111.3, 112.2, 115.1 q (C^2, J_{C-F} 2.2 Hz), 120.8, 121.8, 125.0 q (C^7, J_{C-F} 1.5 Hz), 125.1, 125.3 q (CF_3, J_{C-F} 280.4 Hz), 126.5, 129.0, 137.1 q (J_{C-F} 1.7 Hz), 144.3, 147.4, 149.1, 149.5. ^{19}F NMR ($CDCl_3$, 376 MHz, measured in a mixture with **7c**) δ, ppm: -66.27 dd (CF_3, J_{H-F} 8.9 Hz, J_{H-F} 1.0 Hz). HRMS (MALDI-TOF): $C_{18}H_{15}BrF_3O_2$ found 399.0192 $[M+H]^+$; calcd. 399.0203.

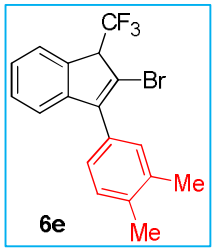


2-Bromo-1-(trifluoromethyl)-6-methyl-3-phenyl-1*H*-indene (6d): Colorless solid, mp 88-90 °C (MeOH). The reaction scale is 60 mg (0.16 mmol) alcohol **1b** and 624 mg (8.0 mmol) benzene, isolated amount is 34 mg **6d** (yield 60%). ^1H



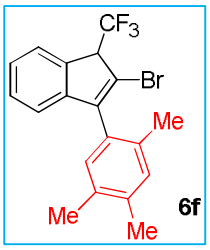
NMR ($CDCl_3$, 400 MHz) δ, ppm: 2.42 s (3H, CH_3), 4.30 q (1H, C^1H, $^3J_{H-F}$ 8.5 Hz), 7.13-7.18 m ($2H_{arom.}$), 7.42-7.52 m ($6H_{arom.}$). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 21.7 (CH_3), 56.8 q (C^1, J_{C-F} 28.9 Hz), 114.3 q (C^2, J_{C-F} 2.4 Hz), 120.5, 125.3 q (CF_3, J_{C-F} 280.2 Hz), 125.9 q (C^7, J_{C-F} 1.3 Hz), 128.7, 128.8, 129.0, 129.6 132.9 (C^3), 136.6, 137.3 q (J_{C-F} 1.6 Hz), 141.6, 147.6. ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: -66.29 d (CF_3, J_{H-F} 8.5 Hz). MS (GC-MS, EI), m/z, ($I_{rel.}$, %): 352/354 $[M]^+$ (30/30), 273 (100), 202 (13), 137 (13), 101 (18), 88 (7). HRMS (MALDI-TOF): $C_{17}H_{13}BrF_3$ found 353.0144 $[M+H]^+$; calcd. 353.0147.

2-Bromo-1-(trifluoromethyl)-3-(3,4-dimethylphenyl)-1*H*-indene (6e): The reaction



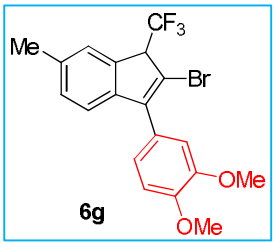
scale is 30 mg (0.08 mmol) dibromoindene **3a** and 10 mg (0.10 mmol) *ortho*-xylene, isolated amount is 22 mg mixture of bromoindene **6e** and indene **7b** in ratio **6e** : **7b** = 7.6:1 (yield **6e** 68%). ^1H NMR ($CDCl_3$, 400 MHz, measured in a mixture with **7b**) δ, ppm: 2.35 s (6H, CH_3), 4.32 q (1H, C^1H, $^3J_{H-F}$ 8.7 Hz), 7.25-7.37 m ($6H_{arom.}$), 7.70 d ($1H_{arom.}$, ^3J 7.5 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz, measured in a mixture with **7b**) δ, ppm: 19.9 (CH_3), 20.0 (CH_3), 56.9 q (C^1, J_{C-F} 29.0 Hz), 115.1 q (C^2, J_{C-F} 2.4 Hz), 120.9, 124.9 q (C^7, J_{C-F} 1.5 Hz), 125.3 q (CF_3, J_{C-F} 280.4 Hz), 126.4, 126.5, 128.9, 130.0, 130.1 (C^3), 137.0, 137.1 q (J_{C-F} 1.7 Hz), 137.5, 144.4, 147.8. ^{19}F NMR ($CDCl_3$, 376 MHz, measured in a mixture with **7b**) δ, ppm: -66.30 dd (CF_3, J_{H-F} 8.7 Hz, J_{H-F} 1.1 Hz). HRMS (MALDI-TOF): $C_{18}H_{15}BrF_3$ found 367.0295 $[M+H]^+$; calcd. 367.0304.

2-Bromo-1-(trifluoromethyl)-3-(2,4,5-trimethylphenyl)-1*H*-indene (6f): The reaction



scale is 30 mg (0.08 mmol) dibromoindene **3a** and 12 mg (0.10 mmol) pseudocumene, isolated amount is 19 mg mixture of bromoindene **6f** and indene **7d** in ratio **6f** : **7d** = 10:1 (yield **6f** 5%). ^1H NMR ($CDCl_3$, 400 MHz) δ, ppm: 2.09 s (3H, CH_3), 2.28 s (3H, CH_3), 2.30 s (3H, CH_3), 4.36 q (1H, C^1H, $^3J_{H-F}$ 8.7 Hz), 6.94-6.98 m ($2H_{arom.}$), 7.11 s ($1H_{arom.}$), 7.28-7.38 m ($2H_{arom.}$), 7.60 d ($1H_{arom.}$, ^3J 6.8 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: -66.43 dd (CF_3, J_{H-F} 8.7 Hz, J_{H-F} 1.0 Hz). HRMS (MALDI-TOF): $C_{19}H_{17}BrF_3$ found 381.0465 $[M+H]^+$; calcd. 381.0461.

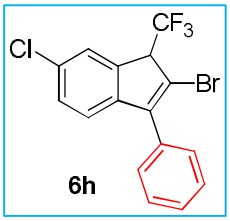
2-Bromo-1-(trifluoromethyl)-3-(3,4-dimethoxyphenyl)-6-methyl-1*H*-indene (6g): Pale



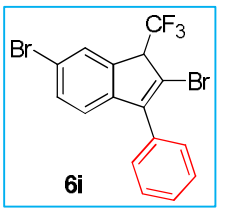
yellow oil. The reaction scale is 30 mg (0.08 mmol) dibromoindene **3b** and 12 mg (0.09 mmol) veratrole, isolated amount is 14 mg **6g** (yield 41%). ^1H NMR ($CDCl_3$, 400 MHz) δ, ppm: 2.41 s (3H, CH_3), 3.92 s (3H, CH_3), 3.95 s (3H, CH_3), 4.28 q (1H, C^1H, $^3J_{H-F}$ 8.8 Hz,), 7.00 d ($1H_{arom.}$, ^3J 8.3 Hz), 7.05 d ($1H_{arom.}$, ^4J 1.9 Hz), 7.10 dd ($1H_{arom.}$, ^3J 8.3 Hz, ^4J 1.9 Hz), 7.15-7.20 m ($2H_{arom.}$), 7.42 s ($1H_{arom.}$). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 21.7 (CH_3), 56.1 (CH_3), 56.2 (CH_3), 56.7 q (C^1, J_{C-F} 29.0 Hz), 111.3, 112.2, 113.8 q (C^2, J_{C-F} 2.3 Hz), 120.5, 121.8, 125.3 q (CF_3, J_{C-F} 280.4 Hz), 125.3, 125.9 q (C^7, J_{C-F} 1.3 Hz), 129.6, 136.6, 137.3 q (J_{C-F}

1.4 Hz), 141.6, 147.3, 149.0, 149.5. ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: -66.30 dd (CF_3, J_{H-F} 8.8 Hz, J_{H-F} 1.0 Hz). HRMS (MALDI-TOF): $C_{19}H_{17}BrF_3O_2$ found 413.0347 $[M+H]^+$; calcd. 413.0359.

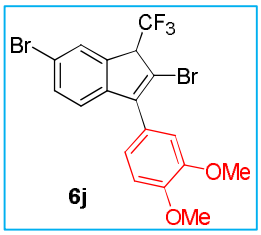
2-Bromo-6-chloro-1-(trifluoromethyl)-3-phenyl-1*H*-indene (6h): The reaction scale is 30 mg (0.08 mmol) dibromoindene **3c** and 312 mg (4.0 mmol) benzene, isolated amount is 14 mg mixture of bromoindene **6h** and indene **7g** in ratio **6h** : **7g** = 9:1 (yield **6h** 42%). ^{1}H NMR ($CDCl_3$, 400 MHz, measured in a mixture with **7g**) δ, ppm: 4.33 q (1H, C^{1}H, $^3J_{H-F}$ 8.6 Hz), 7.17 d (1H, C^{4}H, ^3J 8.2 Hz), 7.34 dd (1H, C^{5}H, ^3J 8.2 Hz, ^3J 1.9 Hz), 7.46-7.52 m (5H$_{arom.}$), 7.59 s (1H, C^{7}H). ^{13}C NMR ($CDCl_3$, 100 MHz, measured in a mixture with **7g**) δ, ppm: 56.8 q (C^1, J_{C-F} 29.3 Hz), 115.8 q (C^2, J_{C-F} 2.3 Hz), 121.6, 124.9 q (CF_3, J_{C-F} 280.7 Hz), 125.6 q (C^7, J_{C-F} 1.7 Hz), 128.8, 128.9, 129.1, 129.3, 132.3, 132.8 (C^3), 138.5 q (J_{C-F} 1.7 Hz), 142.7, 147.1. ^{19}F NMR ($CDCl_3$, 376 MHz, measured in a mixture with **7g**) δ, ppm: -66.17 dd (CF_3, J_{H-F} 8.6 Hz, J_{H-F} 1.0 Hz). HRMS (MALDI-TOF): $C_{16}H_{10}F_3BrCl$ found 372.9593 $[M+H]^+$; calcd. 372.9601.



2,6-Dibromo-1-(trifluoromethyl)-3-phenyl-1*H*-indene (6i): The reaction scale is 30 mg (0.06 mmol) dibromoindene **3d** and 234 mg (3.0 mmol) benzene at 1 h, isolated amount is 13 mg mixture of bromoindene **6i** and indene **7i** in ratio **6i** : **7i** = 3:1 (yield **6i** 42%). ^{1}H NMR ($CDCl_3$, 400 MHz, measured in a mixture with **7i**) δ, ppm: 4.33 q (1H, C^{1}H, $^3J_{H-F}$ 8.4 Hz), 7.11 d (1H$_{arom.}$, ^3J 8.2 Hz), 7.45-7.57 m (6H$_{arom.}$), 7.74 s (1H$_{arom.}$). ^{13}C NMR ($CDCl_3$, 100 MHz, measured in a mixture with **7i**) δ, ppm: 56.8 q (C^1, J_{C-F} 29.3 Hz), 115.9 q (C^2, J_{C-F} 2.2 Hz), 120.7, 122.0, 124.8 q (CF_3, J_{C-F} 280.6 Hz), 125.0 q (C^7, J_{C-F} 1.7 Hz), 127.8, 128.3, 128.9, 128.9, 132.2, 134.1, 138.7 q (J_{C-F} 1.5 Hz), 143.2, 147.2. ^{19}F NMR ($CDCl_3$, 376 MHz, measured in a mixture with **7i**) δ, ppm: -66.12 d (CF_3, J_{H-F} 8.4 Hz). HRMS (MALDI-TOF): $C_{16}H_{10}F_3Br_2$ found 416.9092 $[M+H]^+$; calcd. 416.9096.

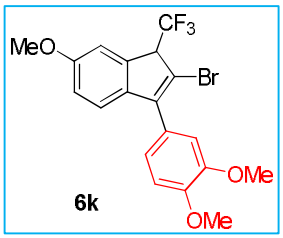


2,6-Dibromo-1-(trifluoromethyl)-3-(3,4-dimethoxyphenyl)-1*H*-indene (6j): The reaction scale is 30 mg (0.06 mmol) dibromoindene **3d** and 10 mg (0.07 mmol) veratrole, isolated amount is 23 mg mixture of bromoindene **6j** and indene **7k** in ratio **6j** : **7k** = 7:1 (yield **6j** 57%). ^{1}H NMR ($CDCl_3$, 400 MHz, measured in a mixture with **7k**) δ, ppm: 3.92 s (3H, CH_3), 3.95 s (3H, CH_3), 4.31 q (1H, C^{1}H, $^3J_{H-F}$ 8.5 Hz), 7.00 d (1H$_{arom.}$, ^3J 8.2 Hz), 7.01 s (1H$_{arom.}$), 7.06 dd (1H$_{arom.}$, ^3J 8.2 Hz, ^4J 2.0 Hz), 7.16 d (1H$_{arom.}$, ^3J 8.2 Hz), 7.51 dd (1H$_{arom.}$, ^3J 8.2 Hz, ^4J 1.6 Hz), 7.74 s (1H$_{arom.}$). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 56.1 (CH_3), 56.2 (CH_3), 56.8 q (C^1, J_{C-F} 29.2 Hz), 111.4, 112.1, 115.3 q (C^2, J_{C-F} 2.4 Hz), 120.7, 121.7, 122.0, 124.6, 124.9 q (CF_3, J_{C-F} 280.4 Hz), 128.3 q (C^7, J_{C-F} 1.3 Hz), 132.2, 138.8 q (J_{C-F} 1.7 Hz),



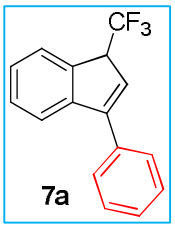
143.2, 146.9, 149.2, 149.8. ^{19}F NMR ($CDCl_3$, 376 MHz, measured in a mixture with **7k**) δ, ppm: -66.11 dd (CF_3, J_{H-F} 8.5 Hz, J_{H-F} 0.8 Hz). HRMS (MALDI-TOF): $C_{18}H_{14}F_3Br_2O_2$ found 476.9307 $[M+H]^+$; calcd. 476.9307.

2-Bromo-1-(trifluoromethyl)-6-methoxy-3-(3,4-dimethoxyphenyl)-1*H*-indene (6k):



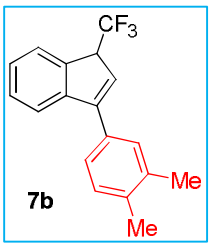
Pale yellow oil. The reaction scale is 30 mg (0.08 mmol) dibromoindene **3e** and 12 mg (0.09 mmol) veratrole, isolated amount is 23 mg **6j** (yield 68%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 3.85 s (3H, CH_3), 3.92 s (3H, CH_3), 3.95 (3H, CH_3), 4.27 q (1H, C^{1}H, $^3J_{H-F}$ 8.6 Hz), 6.88 dd (1H$_{arom.}$, ^3J 8.5 Hz, ^4J 2.3 Hz), 6.99 d (1H$_{arom.}$, ^3J 8.3 Hz), 7.05 d (1H$_{arom.}$, ^4J 1.7 Hz), 7.10 dd (1H$_{arom.}$, ^3J 8.3 Hz, ^4J 1.7 Hz), 7.19-7.21 m (2H$_{arom.}$). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 55.8 (CH_3), 56.1 (CH_3), 56.2 (CH_3), 56.7 q (C^1, J_{C-F} 28.9 Hz), 111.3, 111.8 q (C^2, J_{C-F} 2.3 Hz), 112.1 q (C^7, J_{C-F} 1.6 Hz), 112.2, 113.9, 121.4, 121.8, 125.2 q (CF_3, J_{C-F} 280.4 Hz), 125.4, 137.1, 138.7 q (J_{C-F} 1.6 Hz), 147.0, 149.0, 149.5, 159.0. ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: -66.46 d (CF_3, J 8.6 Hz). HRMS (MALDI-TOF): $C_{19}H_{17}F_3BrO_3$ found 429.0294 $[M+H]^+$; calcd. 429.0308.

1-(Trifluoromethyl)-3-phenyl-1*H*-indene (7a): The reaction scale is 30 mg (0.08 mmol)



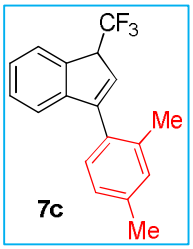
dibromoindene **3a** and 654 mg (8.4 mmol) benzene, isolated amount is 8 mg mixture of bromoindene **6a** and indene **7a** in ratio **6a** : **7a** = 8:1 (yield **7a** 7%). ^{1}H NMR ($CDCl_3$, 400 MHz, measured in a mixture with **6a**) δ, ppm: 4.25 qd (1H, C^{1}H, $^3J_{H-F}$ 9.1 Hz, ^3J 2.1 Hz), 6.43 d (1H, C^{2}H, ^3J 2.1 Hz), 7.24-7.26 m (1H$_{arom.}$), 7.28-7.37 m (2H$_{arom.}$), 7.40-7.49 m (3H$_{arom.}$), 7.57 d (1H$_{arom.}$, ^3J 7.5 Hz), 7.59-7.62 m (1H$_{arom.}$), 7.67 d (1H$_{arom.}$, ^3J 7.5 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz, measured in a mixture with **6a**) δ, ppm: -67.28 d (CF_3, J_{H-F} 9.1 Hz). MS (GC-MS, EI), m/z, ($I_{rel.}$, %): 260 $[M]^+$ (100), 191 (80), 165 (10), 130 (5), 110 (5), 95 (38), 82 (25), 63 (5). HRMS (MALDI-TOF): $C_{16}H_{12}F_3$ found 261.0893 $[M+H]^+$; calcd. 261.0886.

1-(Trifluoromethyl)-3-(3,4-dimethylphenyl)-1*H*-indene (7b): The reaction scale is 30



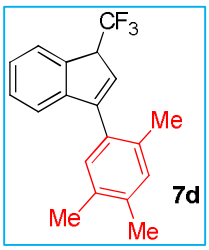
mg (0.08 mmol) dibromoindene **3a** and 10 mg (0.10 mmol) *ortho*-xylene, isolated amount is 22 mg mixture of bromoindene **6e** and indene **7b** in ratio **6e** : **7b** = 7.6:1 (yield **7b** 9%). ^{1}H NMR ($CDCl_3$, 400 MHz, measured in a mixture with **6e**) δ, ppm: 2.35 s (6H, CH_3), 4.23 dq (1H, C^{1}H, $^3J_{H-F}$ 9.5 Hz, ^3J 2.2 Hz), 6.38 d (1H, C^{2}H, ^3J 2.2 Hz), 7.23-7.43 m (5H$_{arom.}$), 7.57-7.61 m (1H$_{arom.}$), 7.66 d (1H$_{arom.}$, ^3J 7.5 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz, measured in a mixture with **6e**) δ, ppm: -67.32 d (CF_3, J_{H-F} 9.5 Hz). HRMS (MALDI-TOF): $C_{18}H_{16}F_3$ found 289.1204 $[M+H]^+$; calcd. 289.1199.

1-(Trifluoromethyl)-3-(2,4-dimethylphenyl)-1*H*-indene (7c): Pale yellow oil. The



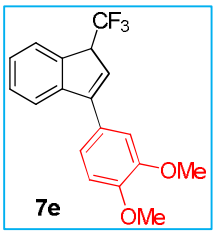
reaction scale is 30 mg (0.08 mmol) dibromoindene **3a** and 10 mg (0.10 mmol) *metha*-xylene, isolated amount is 10 mg **7c** (yield 45%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 2.22 s (3H, CH_3), 2.39 s (3H, CH_3), 4.28 qd (1H, C^{1}H, $^{3}J_{H\text{-}F}$ 9.3 Hz, ^{3}J 2.0 Hz), 6.26 d (1H, C^{2}H, ^{3}J 2.0 Hz), 7.08 d (1H$_{arom.}$, ^{3}J 7.7 Hz), 7.11 d (1H$_{arom.}$, ^{3}J 7.4 Hz), 7.14 s (1H$_{arom.}$), 7.17 d (1H$_{arom.}$, ^{3}J 7.7 Hz), 7.30 td (1H, 1H$_{arom.}$, ^{3}J 7.4 Hz, ^{4}J 1.0 Hz), 7.35 td (1H, 1H$_{arom.}$, ^{3}J 7.4 Hz, ^{4}J 1.0 Hz), 7.65 d (1H$_{arom.}$, ^{3}J 7.4 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 20.1 (CH_3), 21.3 (CH_3), 53.0 q (C^{1}, $J_{C\text{-}F}$ 29.4 Hz), 121.4, 124.7 q (C^{7}, $J_{C\text{-}F}$ 0.8 Hz), 125.8 q (C^{2}, $J_{C\text{-}F}$ 2.7 Hz), 126.2, 126.3 q (CF_3, $J_{C\text{-}F}$ 278.5 Hz), 126.6, 128.5, 129.2, 131.2, 131.3, 136.2, 138.0 q ($J_{C\text{-}F}$ 2.1 Hz), 138.1, 145.7, 149.5. ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: -67.45 d (CF_3, $J_{H\text{-}F}$ 9.3 Hz). HRMS (MALDI-TOF): $C_{18}H_{16}F_3$ found 289.1196 $[M+H]^+$; calcd. 289.1199.

1-(Trifluoromethyl)-3-(2,4,5-trimethylphenyl)-1*H*-indene (7d): The reaction scale is



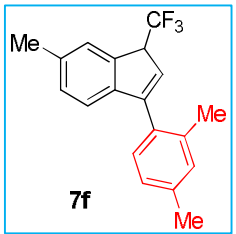
30 mg (0.08 mmol) dibromoindene **3a** and 12 mg (0.10 mmol) pseudocumene, isolated amount is 19 mg mixture of bromoindene **6f** and indene **7d** in ratio **6f** : **7d** = 10:1 (yield **7d** 65%). ^{1}H NMR ($CDCl_3$, 400 MHz, measured in a mixture with **6f**) δ, ppm: 2.19 s (3H, CH_3), 2.27 s (3H, CH_3), 2.30 s (3H, CH_3), 4.28 qd (1H, C^{1}H, $^{3}J_{H\text{-}F}$ 9.3 Hz, ^{3}J 2.0 Hz), 6.25 d (1H, C^{2}H, ^{3}J 2.0 Hz), 7.06 s (1H$_{arom.}$), 7.10 s (1H$_{arom.}$), 7.13 d (1H$_{arom.}$, ^{3}J 7.2 Hz), 7.29-7.38 m (2H$_{arom.}$), 7.66 d (1H$_{arom.}$, ^{3}J 7.2 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 19.3 (CH_3), 19.5 (CH_3), 19.6 (CH_3), 53.0 q (C^{1}, $J_{C\text{-}F}$ 29.4 Hz), 121.5, 124.7 q (C^{7}, $J_{C\text{-}F}$ 0.6 Hz), 125.6 q (C^{2}, $J_{C\text{-}F}$ 2.8 Hz), 126.2, 126.3 q (CF_3, $J_{C\text{-}F}$ 278.4 Hz), 128.5, 130.4, 131.6, 131.9, 133.5, 134.0, 136.7, 138.1 q ($J_{C\text{-}F}$ 2.0 Hz), 145.8, 149.6. ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: -67.45 d (CF_3, $J_{H\text{-}F}$ 9.3 Hz, measured in a mixture with **6f**). HRMS (MALDI-TOF): $C_{19}H_{18}F_3$ found 303.1347 $[M+H]^+$; calcd. 303.1355.

1-(Trifluoromethyl)-3-(3,4-dimethoxyphenyl)-1*H*-indene (7e): The reaction scale is 30



mg (0.08 mmol) dibromoindene **3a** and 14 mg (0.10 mmol) veratrole, isolated amount is 16 mg a mixture of **6c** and **7e** in ratio **6c** : **7e** = 11.5 : 1 (yield **7e** 8%). ^{1}H NMR ($CDCl_3$, 400 MHz, measured in a mixture with **6c**) δ, ppm: 3.95 s (3H, CH_3), 3.96 s (3H, CH_3), 4.24 dq (1H, C^{1}H, $^{3}J_{H\text{-}F}$ 9.5 Hz, ^{3}J 2.2 Hz), 6.37 d (1H, C^{2}H, ^{3}J 2.2 Hz), 6.97 d (1H$_{arom.}$, ^{3}J 8.3 Hz), 7.18 dd (1H$_{arom.}$, ^{3}J 8.3 Hz, ^{4}J 1.9 Hz), 7.28-7.43 m (3H$_{arom.}$), 7.57-7.68 m (2H$_{arom.}$). ^{19}F NMR ($CDCl_3$, 376 MHz, measured in a mixture with **6c**) δ, ppm: -67.30 d (CF_3, $J_{H\text{-}F}$ 9.5 Hz). HRMS (MALDI-TOF): $C_{18}H_{16}F_3O_2$ found 321.1079 $[M+H]^+$; calcd. 321.1097.

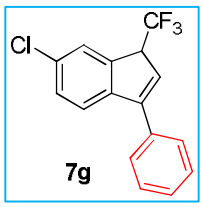
1-(Trifluoromethyl)-3-(2,4-dimethylphenyl)-6-methyl-1*H*-indene



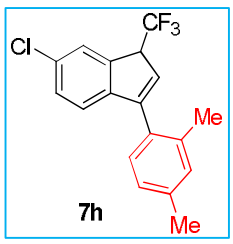
(7f): Pale yellow oil. The reaction scale is 30 mg (0.08 mmol) dibromoindene

3b and 10 mg (0.10 mmol) *metha*-xylene, isolated amount is 10 mg **7f** (yield 39%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 2.21 s (3H, CH_3), 2.38 s (3H, CH_3), 2.43 s (3H, CH_3), 4.23 qd (1H, C^1H, $^{3}J_{H\text{-}F}$ 9.3 Hz, ^{3}J 2.0 Hz), 6.18 d (1H, C^2H, ^{3}J 2.0 Hz), 6.99 d ($1H_{arom.}$, ^{3}J 7.7 Hz), 7.07 d ($1H_{arom.}$, ^{3}J 8.5 Hz), 7.13 s ($1H_{arom.}$), 7.15-7.17 m ($2H_{arom.}$), 7.47 s (1H, C^7H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 20.1 (CH_3), 21.3 (CH_3), 21.6 (CH_3), 52.8 q (C^1, $J_{C\text{-}F}$ 29.3 Hz), 121.1, 124.8 q (C^2, $J_{C\text{-}F}$ 2.7 Hz), 125.6 q (C^7, $J_{C\text{-}F}$ 0.5 Hz), 126.4 q (CF_3, $J_{C\text{-}F}$ 278.5 Hz), 126.6, 129.1, 129.2, 131.3, 131.5, 136.1, 136.2, 138.0, 138.3 q ($J_{C\text{-}F}$ 1.8 Hz), 143.2, 149.3. ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: -67.47 d (CF_3, $J_{H\text{-}F}$ 9.3 Hz). HRMS (MALDI-TOF): $C_{19}H_{18}F_3$ found 303.1368 $[M+H]^+$; calcd. 303.1356.

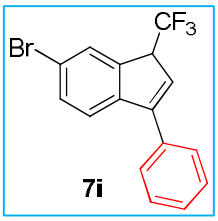
6-Chloro-1-(trifluoromethyl)-3-phenyl-1*H*-indene (7g): The reaction scale is 30 mg (0.08 mmol) dibromoindene **3c** and 312 mg (4.0 mmol) benzene, isolated amount is 14 mg mixture of bromoindene **6h** and indene **7g** in ratio **6h** : **7g** = 9:1 (yield **7g** 6%). ^{1}H NMR ($CDCl_3$, 400 MHz, measured in a mixture with **6h**) δ, ppm: 4.24 qd (1H, C^1H, $^{3}J_{H\text{-}F}$ 9.2 Hz, ^{3}J 2.2 Hz), 6.42 d (1H, C^2H, ^{3}J 2.2 Hz), 7.23 d (1H, C^4H, ^{3}J 8.2 Hz), 7.40 dd (1H, C^5H, ^{3}J 8.2 Hz, ^{3}J 1.9 Hz), 7.43-7.59 m ($5H_{arom.}$), 7.64 s (1H, C^7H). ^{19}F NMR ($CDCl_3$, 376 MHz, measured in a mixture with **6h**) δ, ppm: -67.23 d (CF_3, $J_{H\text{-}F}$ 9.2 Hz). HRMS (MALDI-TOF): $C_{16}H_{11}F_3Cl$ found 295.0499 $[M+H]^+$; calcd. 295.0496.



6-Chloro-1-(trifluoromethyl)-3-(2,4-dimethylphenyl)-1*H*-indene (7h): Pale yellow oil. The reaction scale is 30 mg (0.08 mmol) dibromoindene **3c** and 10 mg (0.10 mmol) *metha*-xylene, isolated amount is 20 mg **7h** (yield 78%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 2.20 s (3H, CH_3), 2.38 s (3H, CH_3), 4.27 qd (1H, C^1H, $^{3}J_{H\text{-}F}$ 9.2 Hz, ^{3}J 2.0 Hz), 6.26 d (1H, C^2H, ^{3}J 2.0 Hz), 7.02 d (1H, C^4H, ^{3}J 8.1 Hz), 7.08 d ($1H_{arom.}$, ^{3}J 8.1 Hz), 7.13-7.15 m ($2H_{arom.}$), 7.33 dd (1H, C^5H, ^{3}J 8.1 Hz, ^{4}J 1.8 Hz), 7.63 s (1H, C^7H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 20.0 (CH_3), 21.3 (CH_3), 52.9 q (C^1, $J_{C\text{-}F}$ 29.7 Hz), 122.3, 125.3 q (C^7, $J_{C\text{-}F}$ 0.7 Hz), 125.9 q (CF_3, $J_{C\text{-}F}$ 278.6 Hz), 126.0 q (C^2, $J_{C\text{-}F}$ 2.7 Hz), 126.7, 128.8, 129.0, 130.7, 131.4, 132.5, 136.1, 138.4, 139.6 q ($J_{C\text{-}F}$ 2.1 Hz), 144.3 q ($J_{C\text{-}F}$ 0.4 Hz), 148.9. ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: -67.40 d (CF_3, $J_{H\text{-}F}$ 9.2 Hz). HRMS (MALDI-TOF): $C_{18}H_{15}F_3Cl$ found 323.0811 $[M+H]^+$; calcd. 323.0809.

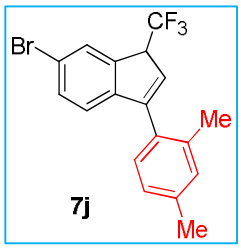


6-Bromo-1-(trifluoromethyl)-3-phenyl-1*H*-indene (7i): The reaction scale is 30 mg (0.06 mmol) dibromoindene **3d** and 234 mg (3.0 mmol) benzene at 1 h, isolated amount is 13 mg mixture of bromoindene **6i** and indene **7i** in ratio **6i** : **7i** = 3:1 (yield **7i** 17%). ^{1}H NMR ($CDCl_3$, 400 MHz, measured in a mixture with **6i**) δ, ppm: 4.24 qd (1H, C^1H, $^{3}J_{H\text{-}F}$ 9.0 Hz, ^{3}J 2.0 Hz), 6.45 d (1H, C^2H, ^{3}J 2.0 Hz), 7.42 d ($1H_{arom.}$, ^{3}J 8.3 Hz), 7.45-7.57 m ($6H_{arom.}$), 7.79 s ($1H_{arom.}$). ^{13}C NMR ($CDCl_3$, 100 MHz, measured in a mixture with **6i**) δ, ppm: 52.7 q (C^1, $J_{C\text{-}F}$ 29.9 Hz), 120.6, 122.5, 125.8 q



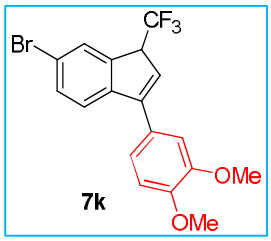
(CF_3, J_{C-F} 278.7 Hz), 128.3, 128.9, 129.0, 129.2, 131.0 q (J_{C-F} 3.3 Hz), 131.7, 132.2, 140.7 q (J_{C-F} 2.0 Hz), 143.3, 148.9. ^{19}F NMR ($CDCl_3$, 376 MHz, measured in a mixture with **6i**) δ, ppm: -67.18 d (CF_3, J_{H-F} 9.0 Hz). HRMS (MALDI-TOF): $C_{16}H_{11}F_3Br$ found 338.9987 $[M+H]^+$; calcd. 338.9991.

6-Bromo-1-(trifluoromethyl)-3-(2,4-dimethylphenyl)-1*H*-indene (7j): Pale yellow oil.



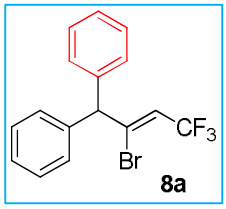
The reaction scale is 30 mg (0.06 mmol) dibromoindene **3d** and 7 mg (0.07 mmol) *metha*-xylene, isolated amount is 18 mg **7j** (yield 88%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 2.19 s (3H, CH_3), 2.38 s (3H, CH_3), 4.26 qd (1H, C^1H, $^3J_{H-F}$ 9.2 Hz, ^3J 2.0 Hz), 6.25 d (1H, C^2H, ^3J 2.0 Hz), 6.97 d (1H, C^4H, ^3J 8.1 Hz), 7.08 d (1$H_{arom.}$, ^3J 7.7 Hz), 7.14 s (1$H_{arom.}$), 7.14 d (1$H_{arom.}$, ^3J 7.7 Hz), 7.49 dd (1H, C^5H, ^3J 8.1 Hz, ^4J 1.7 Hz), 7.78 s (1H, C^7H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 20.0 (CH_3), 21.3 (CH_3), 52.9 q (C^1, J_{C-F} 29.8 Hz), 120.4, 122.7, 125.9 q (CF_3, J_{C-F} 278.6 Hz), 126.1 q (C^2, J_{C-F} 2.7 Hz), 126.7, 128.1 q (C^7, J_{C-F} 0.8 Hz), 129.1, 130.7 (C^3), 131.4, 131.7, 136.1, 138.4, 139.9 q (J_{C-F} 2.1 Hz), 144.7, 149.0. ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: -67.34 d (CF_3, J_{H-F} 9.2 Hz). HRMS (MALDI-TOF): $C_{18}H_{15}F_3Br$ found 367.0297 $[M+H]^+$; calcd. 367.0304.

6-Bromo-1-(trifluoromethyl)-3-(3,4-dimethoxyphenyl)-1*H*-indene (7k): The reaction



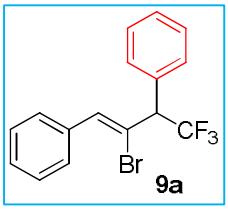
scale is 30 mg (0.06 mmol) dibromoindene **3d** and 10 mg (0.07 mmol) veratrole, isolated amount is 23 mg mixture of bromoindene **6j** and indene **7k** in ratio **6j** : **7k** = 7:1 (yield **7k** 57%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 3.94 s (3H, CH_3), 3.94 s (3H, CH_3), 4.22 qd (1H, C^1H, $^3J_{H-F}$ 9.2 Hz, ^3J 2.3 Hz), 6.35 d (1H, C^2H, ^3J 2.3 Hz), 6.97 d (1$H_{arom.}$, ^3J 8.3 Hz), 7.05-7.08 m (1$H_{arom.}$), 7.13-7.15 m (1$H_{arom.}$), 7.43 d (1$H_{arom.}$, ^3J 8.2 Hz), 7.56 dd (1$H_{arom.}$, ^3J 8.2 Hz, ^4J 1.7 Hz), 7.78 s (1$H_{arom.}$). ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: -67.18 d (CF_3, J_{H-F} 9.2 Hz). HRMS (MALDI-TOF): $C_{18}H_{15}F_3BrO_2$ found 399.0190 $[M+H]^+$; calcd. 399.0202.

(*Z*)-3-Bromo-1,1,1-trifluoro-4,4-diphenylbut-2-ene (8a) and (*Z*)-3-bromo-1,1,1-trifluoro-2,4-diphenylbut-3-ene (9a): The reaction scale is 60 mg (0.22 mmol) alcohol **2a** and 18 mg (0.24 mmol) benzene, isolated amount is 22 mg **8a** and 42 mg a mixture of **8a** and **9a** (total yield 95%, ratio **8a**:**9a** = 2.7:1).



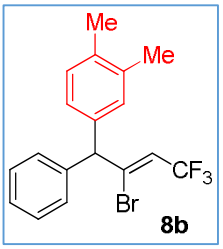
Compound **8a**: Colorless solid, mp 70-73°C (MeOH). ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 5.22 m (1H, C^4H), 5.91 qd (1H, C^2H, $^3J_{H-F}$ 7.2 Hz, ^4J 1.4 Hz), 7.18-7.20 m (4H_{Ph}), 7.30-7.39 m (6H_{Ph}). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 63.1 (C^4), 122.2 q (C^1, J_{C-F} 271.0 Hz), 123.0 q (C^2, J_{C-F} 36.0 Hz), 127.9, 129.0, 129.3, 139.2, 140.1 q (C^3, J_{C-F} 6.0 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: -59.15 dd (CF_3, J_{H-F} 7.2 Hz, J_{H-F} 2.1 Hz). MS (GC-MS, EI), m/z, ($I_{rel.}$, %): 340/342 $[M]^+$ (53/50), 261 (74), 241 (12), 221 (18), 191 (45), 183 (61), 167 (100), 152

(24), 133 (29), 115 (36), 110 (30), 95 (30), 77 (18), 63 (18), 51 (32).HRMS (MALDI-TOF): $C_{16}H_{13}BrF_3$ found 341.0149 $[M+H]^+$; calcd. 341.0147. Compound **9a**: ^{1}H NMR ($CDCl_3$, 400 MHz, measured in a mixture with **8a**) δ, ppm: 4.57 q (1H, C^2H, $^3J_{H-F}$ 8.9 Hz), 7.25 s (1H, C^4H), 7.30-7.48 m ($6H_{Ph}$), 7.47-7.49 m ($2H_{Ph}$), 7.60-7.62 m ($2H_{Ph}$). ^{13}C NMR ($CDCl_3$, 100 MHz, measured in a mixture with **8a**) δ, ppm: 60.9 q (C^2, J_{C-F} 27.9 Hz), 118.7 q (C^3, J_{C-F} 1.7 Hz), 125.2 q (C^1, J_{C-F} 281.7 Hz), 128.4, 128.6, 128.9, 129.0, 129.3, 129.5 q (J_{C-F} 0.4 Hz), 132.7 q (C^4, J_{C-F} 1.4 Hz), 132.9 q (J_{C-F} 0.5 Hz), 135.4. ^{19}F NMR ($CDCl_3$, 376 MHz, measured in a mixture with **8a**) δ, ppm: -65.38 d (CF_3, J_{H-F} 8.9 Hz). MS (GC-MS, EI), m/z, ($I_{rel.}$, %): 340/342 $[M]^+$ (79/80), 261 (62), 221 (12), 191 (100), 183 (72), 165 (21), 133 (22), 115 (23), 109 (32), 95 (59), 82 (30), 63 (17), 51 (25). HRMS (MALDI-TOF): $C_{16}H_{13}BrF_3$ found 341.0149 $[M+H]^+$; calcd. 341.0147.

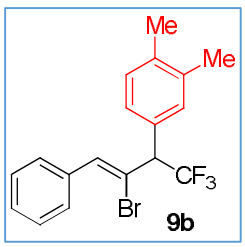


9a

(*Z*)-3-Bromo-1,1,1-trifluoro-4-(3,4-dimethylphenyl)-4-penylbut-2-ene (8b) and (*Z*)-3-bromo-1,1,1-trifluoro-2-(3,4-dimethylphenyl)-4-phenylbut-3-ene (9b): The reaction scale is 60 mg (0.22 mmol) alcohol **2a** and 26 mg (0.24 mmol) *ortho*-xylene, isolated amount is 28 mg **8b** and 32 mg a mixture of **8b** and **9b** (total yield 74%, ratio **8b** : **9b** = 1.3:1). Compound **8b**: Pale yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 2.24 s (3H, CH_3), 2.25 s (3H, CH_3), 5.14 m (1H, C^4H), 5.91 qd (1H, C^2H, $^3J_{H-F}$ 7.2 Hz, ^4J 1.2 Hz), 6.90 d ($1H_{arom.}$, ^3J 7.7 Hz), 6.93 s ($1H_{arom.}$), 7.11 d ($1H_{arom.}$, ^3J 7.7 Hz), 7.18 d ($2H_{arom.}$, ^3J 7.0 Hz), 7.30 d ($1H_{arom.}$, ^3J 7.1 Hz), 7.34 d ($2H_{arom.}$, ^3J 7.5 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 19.6 (CH_3), 20.0 (CH_3), 62.8 (C^4), 122.3 q (C^1, J_{C-F} 271.0 Hz), 122.7 q (C^2, J_{C-F} 35.9 Hz), 126.5, 127.7, 129.0, 129.2, 130.2, 130.5, 136.3, 136.6, 137.3, 139.6, 140.5 q (C^3, J_{C-F} 6.1 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: -59.07 dd (CF_3, J_{H-F} 7.2 Hz, J_{H-F} 2.1 Hz). MS (GC-MS, EI), m/z, ($I_{rel.}$, %): 368/370 (84/83) $[M]^+$, 353/355 (5/4), 289 (81), 274 (14), 249 (8), 219 (17), 211 (23), 195 (100), 183 (62), 180 (32), 165 (33), 133 (15), 115 (13), 101 (17), 91 (28), 77 (16), 51 (6). HRMS (MALDI-TOF): $C_{18}H_{17}BrF_3$ found 369.0461 $[M+H]^+$; calcd. 369.0460. Compound **9b**: ^{1}H NMR ($CDCl_3$, 400 MHz, measured in a mixture with **8b**) δ, ppm: 2.28 s (3H, CH_3), 2.30 s (3H, CH_3), 4.49 q (1H, C^2H, $^3J_{H-F}$ 9.0 Hz), 7.16-7.22 m ($3H_{arom.}$), 7.22 s (1H, C^4H), 7.33-7.43 m ($3H_{arom.}$), 7.60 d ($2H_{arom.}$, ^3J 7.2 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz, measured in a mixture with **8b**) δ, ppm: 19.7 (CH_3), 20.0 (CH_3), 60.6 q (C^2, J_{C-F} 27.8 Hz), 119.1 q (C^3, J_{C-F} 1.5 Hz), 125.2 q (C^1, J_{C-F} 281.6 Hz), 126.7, 128.3, 128.5, 129.3, 130.1, 130.2, 130.7, 132.3 q (C^4, J_{C-F} 1.4 Hz), 135.6, 137.2, 137.5. ^{19}F NMR ($CDCl_3$, 376 MHz, measured in a mixture with **8b**) δ, ppm: -65.45 d (CF_3, J 9.0 Hz). MS (GC-MS, EI), m/z, ($I_{rel.}$, %): 368/370 (97/100) $[M]^+$, 353/355 (5/5), 289 (74), 274 (12), 254 (6), 220



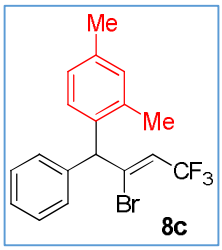
8b



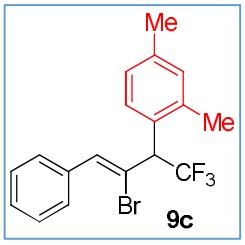
9b

(41), 212 (34), 205 (27), 195 (30), 183 (52), 165 (5), 133 (11), 115 (16), 102 (26), 91 (18), 77 (15), 51 (7). HRMS (MALDI-TOF): $C_{18}H_{17}BrF_3$ found 369.0461 $[M+H]^+$; calcd. 369.0460.

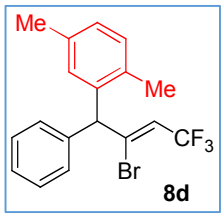
(*Z*)-3-Bromo-1,1,1-trifluoro-4-(2,4-dimethylphenyl)-4-penylbut-2-ene (8c) and (*Z*)-3-bromo-1,1,1-trifluoro-2-(2,4-dimethylphenyl)-4-phenylbut-3-ene (9c): The reaction scale is 60 mg (0.22 mmol) alcohol **2a** and 26 mg (0.24 mmol) *meta*-xylene, isolated amount is 36 mg **8c** and 30 mg **9c** (total yield 81%, ratio **8c** : **9c** = 1.2:1). Compound **8c**: Pale yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 2.23 s (3H, CH_3), 2.32 s (3H, CH_3), 5.28 m (1H, C^4H), 5.81 qd (1H, C^2H, $^3J_{H-F}$ 7.3 Hz, ^4J 1.3 Hz), 6.86 d (1$H_{arom.}$, ^3J 7.9 Hz), 7.00 d (1$H_{arom.}$, ^3J 8.2 Hz), 7.04 s (1$H_{arom.}$), 7.14-7.16 m (2$H_{arom.}$), 7.30-7.35 m (3$H_{arom.}$). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 19.6 (CH_3), 21.1 (CH_3), 59.7 (C^4), 122.3 q (C^1, J_{C-F} 270.8 Hz), 122.6 q (C^2, J_{C-F} 36.0 Hz), 127.1, 127.8, 128.5, 129.0, 129.5, 132.0, 135.0, 136.6, 137.5, 138.8, 140.1 q (C^3, J_{C-F} 6.1 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: -59.13 dd (CF_3, J_{H-F} 7.3 Hz, J_{H-F} 2.1 Hz). MS (GC-MS, EI), m/z, ($I_{rel.}$, %): 368/370 (68/67) $[M]^+$, 289 (53), 211 (19), 195 (100), 183 (34), 165 (22), 115 (12), 91 (15), 77 (13). HRMS (MALDI-TOF): $C_{18}H_{17}BrF_3$ found 369.0460 $[M+H]^+$; calcd. 369.0460.



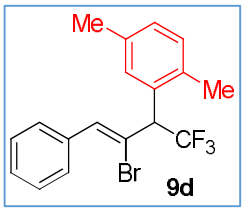
Compound **9c**: Pale yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 2.34 s (3H, CH_3), 2.39 s (3H, CH_3), 4.78 q (1H, C^2H, $^3J_{H-F}$ 8.8 Hz), 7.07-7.08 m (2$H_{arom.}$), 7.17 s (1H, C^4H), 7.33-7.39 m (3$H_{arom.}$), 7.41 d (1$H_{arom.}$, ^3J 8.4 Hz), 7.57 d (2$H_{arom.}$, ^3J 7.1 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 20.0 (CH_3), 21.2 (CH_3), 56.1 q (C^2, J_{C-F} 27.5 Hz), 119.2 q (C^3, J_{C-F} 1.6 Hz), 125.6 q (C^1, J_{C-F} 282.2 Hz), 127.3, 128.2 q (J_{C-F} 1.6 Hz), 128.3, 128.5, 128.7, 129.2, 131.9, 132.4 q (C^4, J_{C-F} 1.2 Hz), 135.6, 137.5, 138.6. ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: -65.15 d (CF_3, J_{H-F} 8.8 Hz). MS (GC-MS, EI), m/z, ($I_{rel.}$, %): 368/370 (58/55) $[M]^+$, 353/355 (9/8), 289 (86), 274 (11), 220 (23), 205 (17), 183 (28), 115 (11), 101 (15), 91 (100), 77 (10), 51 (5). HRMS (MALDI-TOF): $C_{18}H_{17}BrF_3$ found 369.0460 $[M+H]^+$; calcd. 369.0460.



(*Z*)-3-Bromo-1,1,1-trifluoro-4-(2,5-dimethylphenyl)-4-penylbut-2-ene (8d) and (*Z*)-3-bromo-1,1,1-trifluoro-2-(2,5-dimethylphenyl)-4-phenylbut-3-ene (9d): The reaction scale is 60 mg (0.22 mmol) alcohol **2a** and 26 mg (0.24 mmol) *para*-xylene, isolated amount is 14 mg **8d** and 16 mg a mixture of **8d** and **9d** (total yield 37%, ratio **8d** : **9d** = 2.8:1). Compound **8d**: Pale yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 2.22 s (3H, CH_3), 2.28 s (3H, CH_3), 5.29 m (1H, C^4H), 5.80 qd (1H, C^2H, $^3J_{H-F}$ 7.2 Hz, ^4J 1.3 Hz), 6.76 s (1$H_{arom.}$), 7.02 d (1$H_{arom.}$, ^3J 8.0 Hz), 7.09 d (1$H_{arom.}$, ^3J 7.7 Hz), 7.15 d (2$H_{arom.}$, ^3J 8.2 Hz), 7.31-7.38 m (3$H_{arom.}$). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 19.3 (CH_3), 21.3 (CH_3), 60.0 (C^4), 122.3 q (C^1, J_{C-F} 270.9 Hz), 122.7 q (C^2, J_{C-F} 35.9 Hz), 127.8, 128.5, 129.0, 129.1, 129.5, 131.0, 133.6, 135.9, 137.7, 138.7, 140.0 q (C^3,

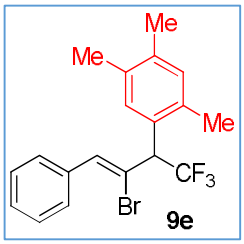


$J_{C\text{-}F}$ 6.1 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: -59.12 dd (CF_3, $J_{H\text{-}F}$ 7.2 Hz, $J_{H\text{-}F}$ 2.2 Hz). MS (GC-MS, EI), m/z, ($I_{rel.}$, %): 368/370 (49/48) $[M]^+$, 289 (41), 274 (6), 211 (16), 195 (42), 183 (26), 180 (16), 165 (16), 115 (11), 105 (15), 91 (100), 77 (14), 51 (5). HRMS (MALDI-TOF): $C_{18}H_{17}BrF_3$ found 369.0458 $[M+H]^+$; calcd. 369.0460. Compound **9d**: ^{1}H NMR ($CDCl_3$, 400 MHz, measured in a mixture with **8d**) δ, ppm: 2.35 s (3H, CH_3), 2.39 s (3H, CH_3), 4.79 q (1H, C^2H, $^3J_{H\text{-}F}$ 8.9 Hz), 7.12 d (2$H_{arom.}$, ^3J 8.1 Hz), 7.17 s (1H, C^4H), 7.31-7.40 m (4$H_{arom.}$), 7.58 d (2$H_{arom.}$, ^3J 7.3 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz, measured in a mixture with **8d**) δ, ppm: 19.5 (CH_3), 21.4 (CH_3), 56.3 q (C^2, $J_{C\text{-}F}$ 27.6 Hz), 119.1 q (C^3, $J_{C\text{-}F}$ 1.6 Hz), 125.5 q (C^1, $J_{C\text{-}F}$ 282.3 Hz), 128.3, 128.5, 128.8 q ($J_{C\text{-}F}$ 1.2 Hz), 129.1, 130.9, 131.4, 132.4 q (C^4, $J_{C\text{-}F}$ 1.4 Hz), 133.6, 134.5, 135.6, 136.0. ^{19}F NMR ($CDCl_3$, 376 MHz, measured in a mixture with **8d**) δ, ppm: -64.96 d (CF_3, $J_{H\text{-}F}$ 8.9 Hz). MS (GC-MS, EI), m/z, ($I_{rel.}$, %): 368/370 (21/20) $[M]^+$, 289 (16), 210 (7), 183 (8), 101 (6), 91 (100), 65 (2). HRMS (MALDI-TOF): $C_{18}H_{17}BrF_3$ found 369.0458 $[M+H]^+$; calcd. 369.0460.



9d

(*Z*)-3-Bromo-1,1,1-trifluoro-4-(2,4,5-trimethylpenyl)-4-phenylbut-2-ene (8e) and (*Z*)-3-bromo-1,1,1-trifluoro-2-(2,4,5-trimethylphenyl)-4-phenylbut-3-ene (9e): The reaction scale is 50 mg (0.18 mmol) alcohol **2a** and 24 mg (0.2 mmol) pseudocumene, isolated amount is 50 mg a mixture of **8e** and **9e** (total yield 73%, ratio **8e** : **9e** = 1.9:1). Compound **8e**: ^{1}H NMR ($CDCl_3$, 400 MHz, measured in a mixture with **9e**) δ, ppm: 2.19 s (3H, CH_3), 2.21 s (3H, CH_3), 2.23 s (3H, CH_3), 5.27 m (1H, C^4H), 5.83 dq (1H, C^2H, $^3J_{H\text{-}F}$ 7.2 Hz, ^4J 1.2 Hz), 6.71 s (1$H_{arom.}$), 6.99 s (1$H_{arom.}$), 7.16 d (2$H_{arom.}$, ^3J 7.2 Hz), 7.31-7.40 m (3$H_{arom.}$). ^{13}C NMR ($CDCl_3$, 100 MHz, measured in a mixture with **9e**) δ, ppm: 19.1 (CH_3), 19.4 (CH_3), 19.6 (CH_3), 59.8 (C^4), 122.3 q (C^1, $J_{C\text{-}F}$ 270.9 Hz), 122.5 q (C^2, $J_{C\text{-}F}$ 35.9 Hz), 127.7, 129.0, 129.5, 129.7, 132.5, 133.9, 134.4, 135.2, 136.1, 138.9, 140.2 q (C^3, $J_{C\text{-}F}$ 5.9 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz, measured in a mixture with **9e**) δ, ppm: -59.06 dd (CF_3, $J_{H\text{-}F}$ 7.2 Hz, $J_{H\text{-}F}$ 2.1 Hz). MS (GC-MS, EI), m/z, ($I_{rel.}$, %): 382/384 (90/88) $[M]^+$, 367/369 (5), 303 (45), 288 (16), 273 (5), 225 (16), 209 (33), 183 (50), 165 (5), 141 (10), 119 (22), 91 (100), 77 (12), 51 (5). HRMS (MALDI-TOF): $C_{19}H_{19}BrF_3$ found 383.0615 $[M+H]^+$; calcd. 383.0617. Compound **9e**: ^{1}H NMR ($CDCl_3$, 400 MHz, measured in a mixture with **8e**) δ, ppm: 2.24 s (3H, CH_3), 2.26 s (3H, CH_3), 2.36 s (3H, CH_3), 4.76 q (1H, C^2H, $^3J_{H\text{-}F}$ 8.9 Hz), 7.02 s (1$H_{arom.}$), 7.17 s (1H, C^4H), 7.25 s (1$H_{arom.}$), 7.30-7.40 m (3$H_{arom.}$), 7.58 d (2$H_{arom.}$, ^3J 7.3 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz, measured in a mixture with **8e**) δ, ppm: 19.4 (CH_3), 19.6 (CH_3), 19.7 (CH_3), 56.1 q (C^2, $J_{C\text{-}F}$ 27.5 Hz), 119.3 q (C^3, $J_{C\text{-}F}$ 1.6 Hz), 125.6 q (C^1, $J_{C\text{-}F}$ 282.2 Hz), 128.3, 128.5, 128.8, 129.2, 129.3 q ($J_{C\text{-}F}$ 1.3 Hz), 132.1 q (C^4, $J_{C\text{-}F}$ 1.5 Hz), 132.4, 134.6, 134.8, 135.6, 137.2. ^{19}F NMR ($CDCl_3$, 376 MHz, measured in a mixture with **8e**)

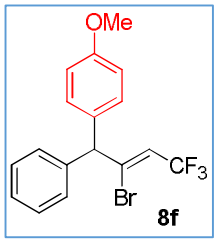


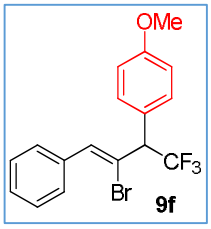
8e

9e

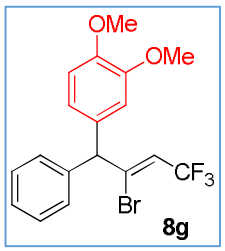
δ, ppm: -65.04 d (CF_3, J_{H-F} 8.9 Hz). MS (GC-MS, EI), m/z, ($I_{rel.}$, %): 382/384 (92/90) $[M]^+$, 367/369 (5), 303 (45), 288 (12), 273 (5), 225 (13), 209 (75), 183 (32), 179 (25), 141 (11), 119 (17), 91 (100), 77 (10), 41 (5). HRMS (MALDI-TOF): $C_{19}H_{19}BrF_3$ found 383.0615 $[M+H]^+$; calcd. 383.0617.

(*Z*)-3-Bromo-1,1,1-trifluoro-4-(4-methoxyphenyl)-4-penylbut-2-ene (8f) and (*Z*)-3-bromo-1,1,1-trifluoro-2-(4-methoxyphenyl)-4-phenylbut-3-ene (9f): The reaction scale is 60 mg (0.22 mmol) alcohol **2a** and 26 mg (0.24 mmol) anisole, isolated amount is 38 mg **8f** and 24 mg a mixture of **8f** and **9f** (total yield 76%, ratio **8f** : **9f** = 4:1). Compound **8f**: Pale yellow solid, mp 46-49°C (MeOH). ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 2.81 s (3H, CH_3), 5.16 m (1H, C^4H), 5.90 qd (1H, C^2H, $^3J_{H-F}$ 7.2 Hz, ^4J 1.0 Hz), 6.89 d ($2H_{arom.}$, ^3J 8.7 Hz), 7.09 d ($2H_{arom.}$, ^3J 8.7 Hz), 7.18 d ($2H_{arom.}$, ^3J 7.1 Hz), 7.31 d ($1H_{arom.}$, ^3J 7.1 Hz), 7.35 d ($2H_{arom.}$, ^3J 7.6 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 55.4 (CH_3), 62.3 (C^4), 114.4, 122.3 q (C^1, J_{C-F} 270.9 Hz), 122.7 q (C^2, J_{C-F} 36.0 Hz), 127.8, 129.0, 129.2, 130.3, 131.3, 139.5, 140.6 q (C^3, J_{C-F} 6.0 Hz), 159.2. ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: -59.10 dd (CF_3, J_{H-F} 7.2 Hz, J_{H-F} 2.0 Hz). MS (GC-MS, EI), m/z, ($I_{rel.}$, %): 370/372 (55/56) $[M]^+$, 291 (35), 271 (5), 221 (6), 197 (100), 183 (34), 178 (8), 165 (13), 135 (8), 111 (5), 77 (7). HRMS (MALDI-TOF): $C_{17}H_{15}BrF_3O$ found 371.0254 $[M+H]^+$; calcd. 371.0253. Compound **9f**: ^{1}H NMR ($CDCl_3$, 400 MHz, measured in a mixture with **8f**) δ, ppm: 3.83 s (3H, CH_3), 4.49 q (1H, C^2H, $^3J_{H-F}$ 9.0 Hz), 6.93 d ($2H_{arom.}$, ^3J 8.8 Hz), 7.21 s (1H, C^4H), 7.28-7.40 m ($5H_{arom.}$), 7.59 d ($2H_{arom.}$, ^3J 7.3 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz, measured in a mixture with **8f**) δ, ppm: 55.4 (CH_3), 60.2 q (C^2, J_{C-F} 28.0 Hz), 114.3, 119.2 q (C^3, J_{C-F} 1.4 Hz), 124.8, 125.2 q (C^1, J_{C-F} 281.6 Hz), 128.3, 128.6, 129.3, 130.6, 132.3 q (C^4, J_{C-F} 1.5 Hz), 135.5, 160.0. ^{19}F NMR ($CDCl_3$, 376 MHz, measured in a mixture with **8f**) δ, ppm: -65.73 d (CF_3, J_{H-F} 9.0 Hz). MS (GC-MS, EI), m/z, ($I_{rel.}$, %): 370/372 (100/92) $[M]^+$, 301/303 (19/20), 291 (47), 225 (23), 222 (57), 207 (24), 183 (37), 178 (24), 152 (7), 139 (16), 111 (28), 89 (13), 76 (16), 51 (5). HRMS (MALDI-TOF): $C_{17}H_{15}BrF_3O$ found 371.0254 $[M+H]^+$; calcd. 371.0253.

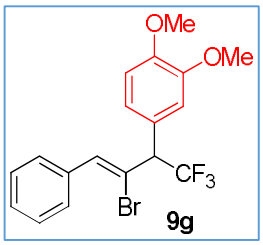




(*Z*)-3-Bromo-1,1,1-trifluoro-4-(3,4-dimethoxypenyl)-4-phenylbut-2-ene (8g) and (*Z*)-3-bromo-1,1,1-trifluoro-2-(3,4-dimethoxyphenyl)-4-phenylbut-3-ene (9g): The reaction scale is 60 mg (0.22 mmol) alcohol **2a** and 24 mg (0.24 mmol) veratrole, isolated amount is 58 mg a mixture of **8g** and **9g** (total yield 66%, ratio **8g** : **9g** = 3:1). Compound **8g**: ^{1}H NMR ($CDCl_3$, 400 MHz, measured in a mixture with **9g**) δ, ppm: 3.83 s (3H, CH_3), 3.88 s (3H, CH_3), 5.15 m (1H, C^4H), 5.91 qd (1H, C^2H, $^3J_{H-F}$ 7.2 Hz, ^4J 1.2 Hz), 6.68 d ($1H_{arom.}$, ^4J 1.9 Hz), 6.70 dd ($1H_{arom.}$, ^3J 8.2 Hz, ^4J 1.9 Hz), 6.84 d ($1H_{arom.}$, ^3J 8.2 Hz), 7.18 d ($2H_{arom.}$, ^3J 7.1 Hz), 7.31-7.38 m ($3H_{arom.}$).



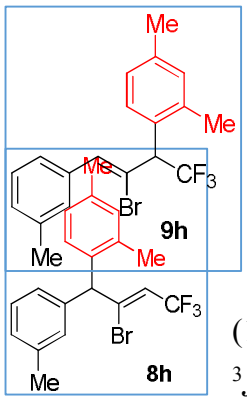
^{13}C NMR ($CDCl_3$, 100 MHz, measured in a mixture with **9g**) δ, ppm: 56.0 (CH_3), 56.0 (CH_3), 62.6 (C^4), 111.4, 112.5, 121.5, 122.3 q (C^1, $J_{C\text{-}F}$ 271.0 Hz), 122.8 q (C^2, $J_{C\text{-}F}$ 35.9 Hz), 127.8, 129.0, 129.1, 131.6, 139.4, 140.4 q (C^3, $J_{C\text{-}F}$ 6.0 Hz), 148.7, 149.3. ^{19}F NMR ($CDCl_3$, 376 MHz, measured in a mixture with **9g**) δ, ppm: -59.11 dd (CF_3, $J_{H\text{-}F}$ 7.2 Hz, $J_{H\text{-}F}$ 2.1 Hz).MS (GC-MS, EI), m/z, ($I_{rel.}$, %): 400/402 (75/80) $[M]^+$, 385/387 (3), 321 (15), 290 (6), 243 (7), 227 (100), 183 (25), 165 (20), 151 (5), 138 (30), 115 (10), 91 (5), 77 (5), 51 (6). HRMS (MALDI-TOF): $C_{18}H_{17}BrF_3O_2$ found 401.0356 $[M+H]^+$; calcd. 401.0359. Compound **9g**: ^{1}H NMR ($CDCl_3$, 400 MHz, measured in a mixture with **8g**) δ, ppm: 3.90 s (6H, CH_3), 4.49 q (1H, C^2H, $^3J_{H\text{-}F}$ 8.9 Hz),



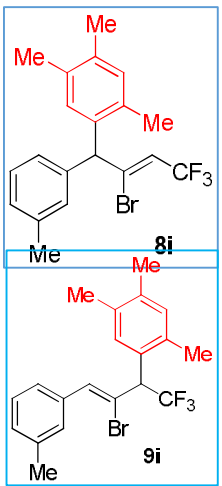
9g

6.89 d ($1H_{arom.}$, ^3J 8.3 Hz), 6.95 s ($1H_{arom.}$), 7.02 dd ($1H_{arom.}$, ^3J 8.3 Hz, ^4J 1.6 Hz), 7.22 s (1H, C^4H), 7.31-7.0 m ($3H_{arom.}$), 7.59 d ($2H_{arom.}$, ^3J 7.2 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz, measured in a mixture with **8g**) δ, ppm: 56.0 (CH_3), 56.1 (CH_3), 60.4 q (C^2, $J_{C\text{-}F}$ 27.9 Hz), 111.3, 112.5, 119.1 q (C^3, $J_{C\text{-}F}$ 1.6 Hz), 122.1, 125.2 q (C^1, $J_{C\text{-}F}$ 281.8 Hz), 125.1 q ($J_{C\text{-}F}$ 0.8 Hz), 128.4, 128.6, 129.2, 132.4 q (C^4, $J_{C\text{-}F}$ 1.4 Hz), 135.5, 149.2, 149.6. ^{19}F NMR ($CDCl_3$, 376 MHz, measured in a mixture with **8g**) δ, ppm: -65.56 d (CF_3, $J_{H\text{-}F}$ 8.9 Hz). MS (GC-MS, EI), m/z, ($I_{rel.}$, %): 400/402 (97/100) $[M]^+$, 385/387 (5), 321 (25), 306 (5), 290 (7), 252 (27), 237 (15), 227 (15), 193 (12), 183 (20), 165 (15), 138 (45), 115 (12), 89 (10), 76 (7), 51 (5). HRMS (MALDI-TOF): $C_{18}H_{17}BrF_3O_2$ found 401.0356 $[M+H]^+$; calcd. 401.0359.

(*Z*)-3-Bromo-1,1,1-trifluoro-4-(2,4-dimethylphenyl)-4-(3-methylphenyl)but-2-ene (8h) and (*Z*)-3-bromo-1,1,1-trifluoro-2-(2,4-dimethylphenyl)-4-(3-methylphenyl)but-3-ene (9h): The reaction scale is 60 mg (0.2 mmol) alcohol **2b** and 12 mg (0.22 mmol) *meta*-xylene, isolated amount is 66 mg a mixture of **8h** and **9h** (total yield 66%, ratio **8h** : **9h** = 1.5:1). Compound **8h**: ^{1}H NMR ($CDCl_3$, 400 MHz, measured in a mixture with **9h**) δ, ppm: 2.24 s (3H, CH_3), 2.31 s (3H, CH_3), 2.34 s (3H, CH_3), 5.24 m (1H, C^4H), 5.81 qd (1H, C^2H, $^{3}J_{H\text{-}F}$ 7.3 Hz, ^{4}J 1.3 Hz), 6.86 d (1$H_{arom.}$, ^{3}J 7.8 Hz), 6.94 d (1$H_{arom.}$, ^{3}J 8.5 Hz), 6.95 s (1$H_{arom.}$), 6.99 d (1$H_{arom.}$, ^{3}J 8.1 Hz), 7.03 s (1$H_{arom.}$), 7.11 d (1$H_{arom.}$, ^{3}J 7.5 Hz), 7.24 t (1$H_{arom.}$, ^{3}J 7.5 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz, measured in a mixture with **9h**) δ, ppm: 19.6 (CH_3), 21.1 (CH_3), 21.6 (CH_3), 59.7 (C^4), 122.3 q (C^1, $J_{C\text{-}F}$ 270.9 Hz), 122.5 q (C^2, $J_{C\text{-}F}$ 35.9 Hz), 126.4, 127.1, 128.5., 128.6, 128.9, 130.2, 131.9, 135.1, 136.6, 137.5, 138.7, 138.7, 140.2 q (C^3, $J_{C\text{-}F}$ 6.0 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz, measured in a mixture with **9h**) δ, ppm: -59.07 dd (CF_3, $J_{H\text{-}F}$ 7.3 Hz, $J_{H\text{-}F}$ 2.2 Hz). MS (GC-MS, EI), m/z, ($I_{rel.}$, %): 382/384 (62) $[M]^+$, 367/369 (3), 303 (55), 287 (10), 263 (5), 233 (10), 209 (100), 194 (25), 165 (5), 142 (12), 128 (15), 105 (26), 77 (12), 65 (7), 51 (5). HRMS (MALDI-TOF): $C_{19}H_{19}BrF_3$ found 383.0619 $[M+H]^+$; calcd. 383.0617. Compound **9h**: ^{1}H NMR ($CDCl_3$, 400 MHz, measured in a mixture with **8h**) δ, ppm: 2.34 s (3H, CH_3), 2.37 s (3H, CH_3), 2.40 s (3H, CH_3), 4.78 qd (1H, C^2H, $^{3}J_{H\text{-}F}$ 8.8 Hz), 7.07-7.14 m (3$H_{arom.}$), 7.14 s (1H, C^4H), 7.24-7.28 m (1$H_{arom.}$), 7.35 s (1$H_{arom.}$), 7.39-7.42 m (2$H_{arom.}$). ^{13}C NMR ($CDCl_3$, 100 MHz, measured in a mixture with **8h**) δ, ppm: 20.0 (CH_3), 21.2 (CH_3), 21.5 (CH_3), 56.1 q (C^2, $J_{C\text{-}F}$ 27.6 Hz), 118.9 q (C^3, $J_{C\text{-}F}$ 1.6 Hz), 125.6 q (C^1, $J_{C\text{-}F}$ 282.0 Hz), 126.2, 127.3, 128.2, 128.2, 128.8, 129.3, 129.9, 131.8, 132.5 q (C^4, $J_{C\text{-}F}$ 1.5 Hz), 135.5, 137.5, 138.0, 138.6. ^{19}F NMR ($CDCl_3$, 376 MHz, measured in a mixture with **8h**) δ, ppm: -65.15 d (CF_3, $J_{H\text{-}F}$ 8.8 Hz). MS (GC-MS, EI), m/z, ($I_{rel.}$, %): 382/384 (38/40) $[M]^+$, 367/369 (5), 303 (50), 288 (5), 223 (16), 211 (26), 197 (22), 142 (7), 128 (9), 105 (100), 89 (7), 77 (9), 51 (5). HRMS (MALDI-TOF): $C_{19}H_{19}BrF_3$ found 383.0619 $[M+H]^+$; calcd. 383.0617.

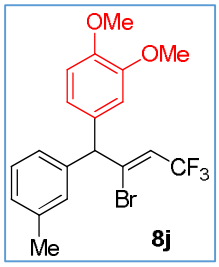


(*Z*)-3-Bromo-1,1,1-trifluoro-4-(2,4,5-trimethylpenyl)-4-(3-methylphenyl)but-2-ene (8i) and (*Z*)-3-bromo-1,1,1-trifluoro-2-(2,4,5-trimethylphenyl)-4-(3-methylphenyl)but-2-ene (9i): The reaction scale is 60 mg (0.2 mmol) alcohol **2b** and 26 mg (0.22 mmol) pseudocumene, isolated amount is 64 mg a mixture of **8i** and **9i** (total yield 81%, ratio **8i** : **9i** = 1.5:1). Compound **8i**: ^{1}H NMR ($CDCl_3$, 400 MHz, measured in a mixture with **9i**) δ, ppm: 2.19 s (3H, CH_3), 2.20 s (3H, CH_3), 2.22 s (3H, CH_3), 2.34 s (3H, CH_3), 5.22 m (1H, C^4H), 5.81 qd (1H, C^2H, $^{3}J_{H\text{-}F}$ 7.3 Hz, ^{4}J 1.1 Hz), 6.70 s (1$H_{arom.}$), 6.94-6.96 m (3$H_{arom.}$), 6.98 s (1$H_{arom.}$), 7.11 d (1$H_{arom.}$, ^{3}J 7.6 Hz), 7.23 d (1$H_{arom.}$, ^{3}J 7.6 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz, measured in a

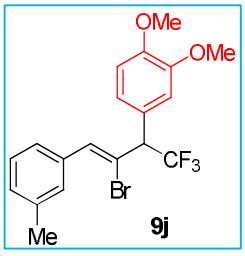


mixture with **9i**) δ, ppm: 19.1 (CH_3), 19.4 (CH_3), 19.6 (CH_3), 21.6 (CH_3), 59.7 (C^4), 122.3 q (C^1, $J_{C\text{-}F}$ 271.0 Hz), 122.4 q (C^2, $J_{C\text{-}F}$ 35.9 Hz), 126.4, 128.5, 128.8, 129.7, 130.3, 132.5, 133.9, 134.4, 135.3, 136.0, 138.7, 138.8, 140.3 q (C^3, $J_{C\text{-}F}$ 6.0 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz, measured in a mixture with **9i**) δ, ppm: -59.02 dd (CF_3, $J_{H\text{-}F}$ 7.3 Hz, $J_{H\text{-}F}$ 2.1 Hz). MS (GC-MS, EI), m/z, ($I_{rel.}$, %): 396/398 $[M]^+$ (55/50), 317 (32), 287 (5), 247 (7), 223 (90), 208 (18), 197 (30), 141 (13), 119 (17), 105 (100), 91 (13), 77 (8), 41 (5). HRMS (MALDI-TOF): $C_{20}H_{21}BrF_3$ found 397.0775 $[M+H]^+$; calcd. 397.0773. Compound **9i**: ^1H NMR ($CDCl_3$, 400 MHz, measured in a mixture with **8i**) δ, ppm: 2.24 s (3H, CH_3), 2.26 s (3H, CH_3), 2.36 s (3H, CH_3), 2.37 s (3H, CH_3), 4.75 q (1H, C^2H, $^3J_{H\text{-}F}$ 8.9 Hz), 7.02 s ($1H_{arom.}$), 7.12-7.14 m (2H, C^4H, $H_{arom.}$), 7.25 s ($1H_{arom.}$), 7.27 d ($1H_{arom.}$, ^3J 7.9 Hz), 7.37 s ($1H_{arom.}$), 7.41 d ($1H_{arom.}$, ^3J 7.9 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz, measured in a mixture with **8i**) δ, ppm: 19.3 (CH_3), 19.5 (CH_3), 19.7 (CH_3), 21.5 (CH_3), 56.1 q (C^2, $J_{C\text{-}F}$ 27.6 Hz), 119.1 q (C^3, $J_{C\text{-}F}$ 1.6 Hz), 125.6 q (C^1, $J_{C\text{-}F}$ 282.3 Hz), 126.2, 128.2, 128.9, 129.2, 129.3 q ($J_{C\text{-}F}$ 1.5 Hz), 129.9, 132.2 q (C^4, $J_{C\text{-}F}$ 1.2 Hz), 132.4, 134.6, 134.8, 135.5, 137.2, 138.0. ^{19}F NMR ($CDCl_3$, 376 MHz, measured in a mixture with **8i**) δ, ppm: -65.06 d (CF_3, $J_{H\text{-}F}$ 8.9 Hz). MS (GC-MS, EI), m/z, ($I_{rel.}$, %): 396/398 $[M]^+$ (23/25), 317 (20), 247 (7), 225 (10), 197 (12), 119 (6), 105 (100), 91 (6), 77 (5). HRMS (MALDI-TOF): $C_{20}H_{21}BrF_3$ found 397.0775 $[M+H]^+$; calcd. 397.0773.

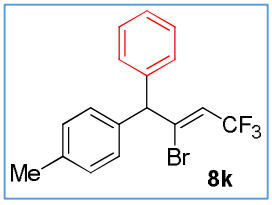
(*Z*)-3-Bromo-1,1,1-trifluoro-4-(3,4-dimethoxyphenyl)-4-(3-methylphenyl)but-2-ene (8j) and (*Z*)-3-bromo-1,1,1-trifluoro-2-(3,4-dimethoxyphenyl)-4-(3-methylphenyl)but-2-ene (9j): The reaction scale is 60 mg (0.2 mmol) alcohol **2b** and 30 mg (0.22 mmol) veratrole, isolated amount is 66 mg a mixture of **8j** and **9j** (total yield 80%, ratio **8j** : **9j** = 2.3:1). Compound **8j**: ^1H NMR ($CDCl_3$, 400 MHz, measured in a mixture with **9j**) δ, ppm: 2.34 s (3H, CH_3), 3.83 s (3H, OCH_3), 3.88 s (3H, OCH_3), 5.11 m (1H, C^4H), 5.91 qd (1H, C^2H, $^3J_{H\text{-}F}$ 7.2 Hz, ^4J 1.2 Hz), 6.68-6.71 m ($2H_{arom.}$), 6.84 d ($1H_{arom.}$, ^3J 8.1 Hz), 6.97-6.98 m ($2H_{arom.}$), 7.12 d ($1H_{arom.}$, ^3J 7.6 Hz), 7.25 t ($1H_{arom.}$, ^3J 7.9 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz, measured in a mixture with **9j**) δ, ppm: 21.6 (CH_3), 56.0 (OCH_3), 56.1 (OCH_3), 62.6 (C^4), 111.4, 112.5, 121.4, 122.3 q (C^1, $J_{C\text{-}F}$ 271.0 Hz), 122.7 q (C^2, $J_{C\text{-}F}$ 35.9 Hz), 126.1, 128.6, 128.8, 129.9, 131.7, 138.7, 139.3, 140.5 q (C^3, $J_{C\text{-}F}$ 6.0 Hz), 148.6, 149.3. ^{19}F NMR ($CDCl_3$, 376 MHz, measured in a mixture with **9j**) δ, ppm: -59.07 dd (CF_3, J 7.2 Hz, J 2.1 Hz). MS (GC-MS, EI), m/z, ($I_{rel.}$, %): 414/416 $[M]^+$ (75/73), 335 (17), 320 (5), 304 (7), 266 (5), 241 (100), 235 (5), 197 (32), 165 (10), 138 (18), 128 (5), 89 (9), 77 (7), 51 (5). HRMS (MALDI-TOF): $C_{19}H_{19}O_2BrF_3$ found 415.0512 $[M+H]^+$; calcd. 415.0515.



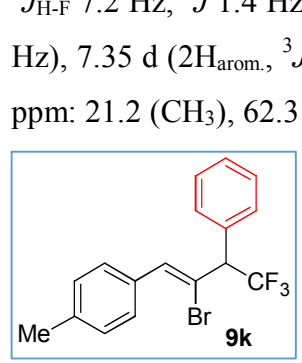
Compound **9j**: ^1H NMR ($CDCl_3$, 400 MHz, measured in a mixture with **8j**) δ, ppm: 2.38 s (3H, CH_3), 3.90 s (6H, OCH_3), 4.48 q (1H, C^2H, $^3J_{H\text{-}F}$ 8.9 Hz), 6.89 d ($1H_{arom.}$, ^3J 8.4 Hz), 6.95 s ($1H_{arom.}$), 7.02 dd ($1H_{arom.}$, ^3J 8.3 Hz,



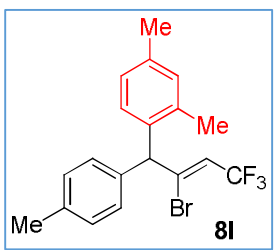
^4J 1.7 Hz), 7.15 d (1H$_{arom.}$, ^3J 7.7 Hz), 7.18 s (1H, C^{4}H), 7.27 t (1H$_{arom.}$, ^3J 7.7 Hz), 7.38 s (1H$_{arom.}$), 7.42 d (1H$_{arom.}$, ^3J 7.8 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz, measured in a mixture with **8j**) δ, ppm: 21.5 (CH_3), 56.0 (OCH_3), 56.1 (OCH_3), 60.4 q (C^2, J_{C-F} 27.9 Hz), 111.3, 112.5, 118.8 q (C^3, J_{C-F} 1.6 Hz), 122.1, 122.4 q (C^1, J_{C-F} 281.3 Hz), 125.2 q (J_{C-F} 0.6 Hz), 126.2, 128.3, 129.3, 129.9, 132.5 q (C^4, J_{C-F} 1.5 Hz), 135.4, 138.0, 149.2, 149.6. ^{19}F NMR ($CDCl_3$, 376 MHz, measured in a mixture with **8j**) δ, ppm: -65.56 d (CF_3, J_{H-F} 8.9 Hz). MS (GC-MS, EI), m/z, (I$_{rel.}$, %): 414/416 [M]$^+$ (100/98), 335 (27), 320 (11), 304 (10), 266 (20), 243 (37), 235 (10), 197 (50), 178 (8), 165 (10), 138 (17), 115 (10), 89 (16), 76 (8), 63 (5), 51 (5). HRMS (MALDI-TOF): $C_{19}H_{19}O_2BrF_3$ found 415.0512 [M+H]$^+$; calcd. 415.0515.



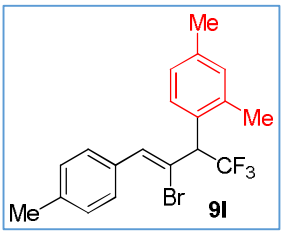
(*Z*)-3-Bromo-1,1,1-trifluoro-4-(4-methylpenyl)-4-phenylbut-2-ene (8k) and (*Z*)-3-bromo-1,1,1-trifluoro-4-(4-methylphenyl)-2-phenylbut-3-ene (9k): The reaction scale is 60 mg (0.2 mmol) alcohol **2c** and 18 mg (0.22 mmol) benzene, isolated amount is 34 mg a mixture of **8k** and **9k** (total yield 48%, ratio **8k** : **9k** = 5:1). Compound **8k**: ^{1}H NMR ($CDCl_3$, 400 MHz, measured in a mixture with **9k**) δ, ppm: 2.35 s (3H, CH_3), 5.17 m (1H, C^{4}H), 5.91 qd (1H, C^{2}H, $^3J_{H-F}$ 7.2 Hz, ^4J 1.4 Hz), 7.06 d (2H$_{arom.}$, ^3J 8.1 Hz), 7.15-7.19 m (4H$_{arom.}$), 7.31 d (1H$_{arom.}$, ^3J 7.1 Hz), 7.35 d (2H$_{arom.}$, ^3J 7.5 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz, measured in a mixture with **9k**) δ, ppm: 21.2 (CH_3), 62.3 (C^4), 122.3 q (C^1, J_{C-F} 270.9 Hz), 122.8 q (C^2, J_{C-F} 36.0 Hz), 127.8, 129.0, 129.1, 129.2, 129.7, 136.2, 137.6, 139.4, 140.4 q (C^3, J_{C-F} 6.1 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz, measured in a mixture with **9k**) δ, ppm: -59.11 dd (CF_3, J_{H-F} 7.2 Hz, J_{H-F} 2.1 Hz). MS (GC-MS, EI), m/z, (I$_{rel.}$, %): 354/356 (67/65) [M]$^+$, 275 (62), 255 (9), 235 (7), 205 (22), 198 (18), 181 (100), 166 (34), 127 (12), 115 (11), 101 (11), 89 (18), 77 (9), 65 (8), 51 (8). HRMS (MALDI-TOF): $C_{17}H_{15}BrF_3$ found 355.0304 [M+H]$^+$; calcd. 355.0304. Compound **9k**: ^{1}H NMR ($CDCl_3$, 400 MHz, measured in a mixture with **8k**) δ, ppm: 2.36 s (3H, CH_3), 4.55 q (1H, C^{2}H, $^3J_{H-F}$ 8.9 Hz), 7.15-7.19 m (3H, C^{4}H, 2H$_{arom.}$), 7.37-7.38 m (1H$_{arom.}$), 7.41 dd (2H$_{arom.}$, ^3J 7.9 Hz), 7.45-7.47 m (2H$_{arom.}$), 7.51 d (2H$_{arom.}$, ^3J 8.1 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz, measured in a mixture with **8k**) δ, ppm: 21.5 (CH_3), 60.9 q (C^2, J_{C-F} 27.8 Hz), 117.8 q (C^3, J_{C-F} 1.4 Hz), 125.2 q (C^1, J_{C-F} 282.0 Hz), 128.8, 128.9, 129.0, 129.2, 129.5, 132.5, 132.6 q (C^4, J_{C-F} 1.5 Hz), 133.0, 138.7. ^{19}F NMR ($CDCl_3$, 376 MHz, measured in a mixture with **8k**) δ, ppm: -65.39 d (CF_3, J_{H-F} 8.9 Hz). MS (GC-MS, EI), m/z, (I$_{rel.}$, %): 354/356 (100/99) [M]$^+$, 285/287 (6/5), 275 (29), 206 (40), 196 (19), 183 (39), 165 (6), 115 (15), 103 (22), 95 (11), 89 (14), 76 (9), 51 (5). HRMS (MALDI-TOF): $C_{17}H_{15}BrF_3$ found 355.0304 [M+H]$^+$; calcd. 355.0304.



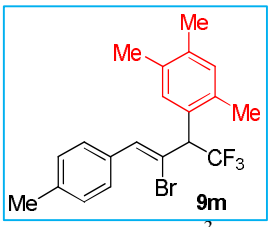
(*Z*)-3-Bromo-1,1,1-trifluoro-4-(4-methylpenyl)-4-(2,4-dimethylphenyl)but-2-ene (8l) and (*Z*)-3-bromo-1,1,1-trifluoro-4-(4-



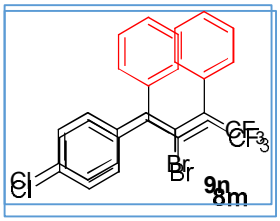
methylphenyl)-2-(2,4-dimethylphenyl)but-3-ene (9l): The reaction scale is 60 mg (0.2 mmol) alcohol **2c** and 24 mg (0.22 mmol) *meta*-xylene, isolated amount is 46 mg a mixture of **8l** and **9l** (total yield 61%, ratio **8l** : **9l** = 1.7:1). Compound **8l**: ^{1}H NMR ($CDCl_3$, 400 MHz, measured in a mixture with **9l**) δ, ppm: 2.22 s (3H, CH_3), 2.31 s (3H, CH_3), 2.35 s (3H, CH_3), 5.24 m (1H, C^4H), 5.81 qd (1H, C^2H, $^{3}J_{H\text{-}F}$ 7.2 Hz, ^{4}J 1.2 Hz), 6.87 d (1$H_{arom.}$, ^{3}J 7.9 Hz), 6.98-7.03 m (4$H_{arom.}$), 7.14-7.17 m (2$H_{arom.}$). ^{13}C NMR ($CDCl_3$, 100 MHz, measured in a mixture with **9l**) δ, ppm: 19.6 (CH_3), 21.1 (CH_3), 21.2 (CH_3), 59.4 (C^4), 122.2 q (C^2, $J_{C\text{-}F}$ 35.8 Hz), 122.3 q (C^1, $J_{C\text{-}F}$ 270.8 Hz), 127.0, 128.4, 129.3, 129.7, 131.9, 135.1, 135.8, 136.5, 137.5, 138.5, 140.4 q (C^3, $J_{C\text{-}F}$ 6.0 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz, measured in a mixture with **9l**) δ, ppm: -59.08 dd (CF_3, $J_{H\text{-}F}$ 7.2 Hz, $J_{H\text{-}F}$ 2.2 Hz). MS (GC-MS, EI), m/z, ($I_{rel.}$, %): 382/384 (70/69) $[M]^+$, 303 (46), 287/289 (10/9), 233 (7), 209 (100), 197 (24), 179 (18), 141 (10), 128 (9), 115 (9), 105 (15), 96 (10), 77 (9). HRMS (MALDI-TOF): $C_{19}H_{19}BrF_3$ found 383.0615 $[M+H]^+$; calcd. 383.0617. Compound **9l**: ^{1}H NMR ($CDCl_3$, 400 MHz, measured in a mixture with **8l**) δ, ppm: 2.33 s (3H, CH_3), 2.35 s (3H, CH_3), 2.39 s (3H, CH_3), 4.76 q (1H, C^2H, $^{3}J_{H\text{-}F}$ 8.9 Hz), 7.06-7.08 m (2$H_{arom.}$), 7.12 s (1H, C^4H), 7.17 d (2$H_{arom.}$, ^{3}J 8.0 Hz), 7.40 d (1$H_{arom.}$, ^{3}J 8.1 Hz), 7.48 d (2$H_{arom.}$, ^{3}J 8.1 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz, measured in a mixture with **8l**) δ, ppm: 19.9 (CH_3), 21.2 (CH_3), 21.5 (CH_3), 56.1 q (C^2, $J_{C\text{-}F}$ 27.4 Hz), 118.3 q (C^3, $J_{C\text{-}F}$ 1.5 Hz), 125.6 q (C^1, $J_{C\text{-}F}$ 282.0 Hz), 127.2, 128.2 q ($J_{C\text{-}F}$ 1.4 Hz), 128.8 q ($J_{C\text{-}F}$ 0.6 Hz), 129.0, 129.2, 131.8, 132.3 q (C^4, $J_{C\text{-}F}$ 1.1 Hz), 132.6, 137.4, 137.5, 138.5. ^{19}F NMR ($CDCl_3$, 376 MHz, measured in a mixture with **8l**) δ, ppm: -65.15 d (CF_3, $J_{H\text{-}F}$ 8.9 Hz). MS (GC-MS, EI), m/z, ($I_{rel.}$, %): 382/384 (55/53) $[M]^+$, 303 (42), 234 (18), 222 (18), 211 (28), 197 (18), 128 (9), 115 (16), 105 (100), 91 (8), 77 (9). HRMS (MALDI-TOF): $C_{19}H_{19}BrF_3$ found 383.0615 $[M+H]^+$; calcd. 383.0617.



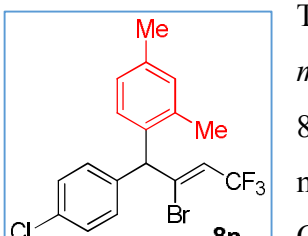
(*Z*)-3-Bromo-1,1,1-trifluoro-4-(4-mehylphenyl)-2-(2,4,5-trimethylphenyl)but-2-ene (9m): Pale yellow oil. The reaction scale is 60 mg (0.2 mmol) alcohol **2c** and 26 mg (0.22 mmol) pseudocumene, isolated amount is 20 mg **9m** (yield 25%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 2.24 s (3H, CH_3), 2.25 s (3H, CH_3), 2.35 s (3H, CH_3), 2.36 s (3H, CH_3), 4.74 q (1H, C^2H, $^{3}J_{H\text{-}F}$ 8.9 Hz), 7.01 s (1$H_{arom.}$), 7.13 s (1H, C^4H), 7.18 d (2$H_{arom.}$, ^{3}J 8.1 Hz), 7.25 s (1$H_{arom.}$), 7.50 d (2$H_{arom.}$, ^{3}J 8.1 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 19.4 (CH_3), 19.5 (CH_3), 19.7 (CH_3), 21.5 (CH_3), 56.1 q (C^2, $J_{C\text{-}F}$ 27.4 Hz), 118.4 q (C^3, $J_{C\text{-}F}$ 1.5 Hz), 125.6 q (C^1, $J_{C\text{-}F}$ 282.0 Hz), 128.9, 129.0, 129.2, 129.3 q ($J_{C\text{-}F}$ 1.4 Hz), 132.0 q (C^4, $J_{C\text{-}F}$ 1.2 Hz), 132.3, 132.7, 134.6, 134.8, 137.2, 138.5. ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: -65.06 d (CF_3, $J_{H\text{-}F}$ 8.9 Hz). MS (GC-MS, EI), m/z, ($I_{rel.}$, %): 396/398 $[M]^+$ (20/19), 317 (15), 248 (7), 225 (7), 197 (8), 115 (8), 105 (100), 91 (5). HRMS (MALDI-TOF): $C_{20}H_{21}BrF_3$ found 397.0776 $[M+H]^+$; calcd. 397.0773.

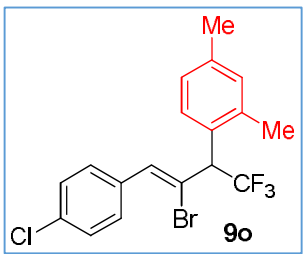


(*Z*)-3-Bromo-4-(4-chloropenyl)-1,1,1-trifluoro-4-phenylbut-2-ene (8m) and (*Z*)-3-bromo-4-(4-chlorophenyl)-1,1,1-trifluoro-2-phenylbut-3-ene (9n): The reaction scale is 60 mg (0.2 mmol) alcohol **2d** and 18 mg (0.22 mmol) benzene, isolated amount is 20 mg **8m** and 38 mg a mixture of **8m** and **9n** (total yield 81%, ratio **8m** : **9n** = 1.6:1). Compound **8m**: Colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 5.18 m (1H, C^4H), 5.90 qd (1H, C^2H, $^3J_{H\text{-}F}$ 7.2 Hz, ^4J 1.3 Hz), 7.12 d ($2H_{arom.}$, ^3J 8.4 Hz), 7.15 dd ($2H_{arom.}$, ^3J 8.3 Hz, ^4J 1.4 Hz), 7.31-7.39 m ($5H_{arom.}$). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 62.3 (C^4), 122.1 q (C^1, $J_{C\text{-}F}$ 271.2 Hz), 123.2 q (C^2, $J_{C\text{-}F}$ 36.1 Hz), 128.1, 129.2, 129.2, 129.3, 130.6, 133.9, 137.7, 138.8, 139.6 q (C^3, $J_{C\text{-}F}$ 5.9 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: -59.22 dd (CF_3, $J_{H\text{-}F}$ 7.2 Hz, $J_{H\text{-}F}$ 2.0 Hz). MS (GC-MS, EI), m/z, ($I_{rel.}$, %): 374/376/378 (74/100/25) $[M]^+$, 295/297 (66/22), 260 (28), 240 (18), 217 (16), 201/203 (93/30), 191 (23), 183 (30), 166 (55), 133 (14), 119 (32), 110 (16), 94 (39), 82 (14), 63 (9), 51 (13). HRMS (MALDI-TOF): $C_{16}H_{12}BrClF_3$ found 374.9760 $[M+H]^+$; calcd. 374.9758. Compound **9n**: ^{1}H NMR ($CDCl_3$, 400 MHz, measured in a mixture with **8m**) δ, ppm: 4.55 q (1H, C^2H, $^3J_{H\text{-}F}$ 8.9 Hz), 7.18 s (1H, C^4H), 7.33-7.37 m ($2H_{arom.}$), 7.41-7.45 m ($5H_{arom.}$), 7.54 d ($1H_{arom.}$, ^3J 8.5 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz, measured in a mixture with **8m**) δ, ppm: 60.9 q (C^2, $J_{C\text{-}F}$ 27.9 Hz), 119.6 q (C^3, $J_{C\text{-}F}$ 1.7 Hz), 125.1 q (C^1, $J_{C\text{-}F}$ 281.9 Hz), 128.6, 128.9, 129.0, 129.4 q ($J_{C\text{-}F}$ 0.7 Hz), 130.6, 131.6 q (C^4, $J_{C\text{-}F}$ 1.1 Hz), 132.7 q ($J_{C\text{-}F}$ 1.2 Hz), 133.8, 134.4. ^{19}F NMR ($CDCl_3$, 376 MHz, measured in a mixture with **8m**) δ, ppm: -65.39 d (CF_3, $J_{H\text{-}F}$ 8.9 Hz). MS (GC-MS, EI), m/z, ($I_{rel.}$, %): 374/376/378 (78/100/25) $[M]^+$, 305/307/309 (7/11/2), 295/297 (39/12), 259 (10), 226 (34), 191 (46), 183 (25), 138 (10), 119 (17), 109 (21), 95 (70), 82 (10), 51 (9). HRMS (MALDI-TOF): $C_{16}H_{12}BrClF_3$ found 374.9760 $[M+H]^+$; calcd. 374.9758.



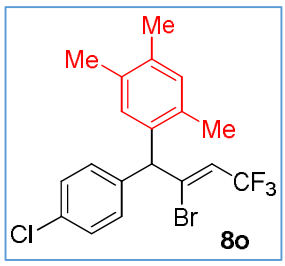
(*Z*)-3-Bromo-4-(4-chloropenyl)-1,1,1-trifluoro-4-(2,4-dimethylphenyl)but-2-ene (8n) and (*Z*)-3-bromo-4-(4-chlorophenyl)-1,1,1-trifluoro-2-(2,4-dimethylphenyl)but-3-ene (9o): The reaction scale is 60 mg (0.2 mmol) alcohol **2d** and 22 mg (0.2 mmol) *meta*-xylene, isolated amount is 62 mg a mixture of **8n** and **9o** (total yield 82%, ratio **8n** : **9o** = 1.5:1). Compound **8n**: ^{1}H NMR ($CDCl_3$, 400 MHz, measured in a mixture with **9o**) δ, ppm: 2.23 s (3H, CH_3), 2.32 s (3H, CH_3), 5.25 m (1H, C^4H), 5.80 qd (1H, C^2H, $^3J_{H\text{-}F}$ 7.2 Hz, ^4J 1.2 Hz), 6.81 d ($1H_{arom.}$, ^3J 7.9 Hz), 7.00 d ($1H_{arom.}$, ^3J 8.0 Hz), 7.05 s ($1H_{arom.}$), 7.09 d ($2H_{arom.}$, ^3J 8.5 Hz), 7.33 d ($2H_{arom.}$, ^3J 8.5 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz, measured in a mixture with **9o**) δ, ppm: 19.6 (CH_3), 21.1 (CH_3), 59.1 (C^4), 122.2 q (C^1, $J_{C\text{-}F}$ 271.0 Hz), 122.8 q (C^2, $J_{C\text{-}F}$ 36.1 Hz), 127.2, 128.4, 129.3, 130.8, 132.1, 133.8, 134.5, 136.5, 137.4, 137.8, 139.5 q (C^3, $J_{C\text{-}F}$ 6.1 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz, measured in a mixture with **9o**) δ, ppm: -59.18 dd (CF_3, $J_{H\text{-}F}$ 7.2 Hz, $J_{H\text{-}F}$ 2.1 Hz). MS (GC-MS, EI), m/z, ($I_{rel.}$, %):

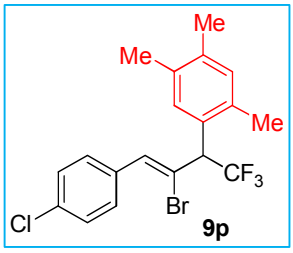




402/404/406 (61/74/19) $[M]^+$, 323/325 (43/13), 288 (13), 229/231 (100/35), 217 (27), 194 (25), 179 (27), 125 (11), 101 (19), 77 (16), 51 (6). HRMS (MALDI-TOF): $C_{18}H_{16}BrClF_3$ found 403.0070 $[M+H]^+$; calcd. 403.0071. Compound **9o**: ^{1}H NMR ($CDCl_3$, 400 MHz, measured in a mixture with **8n**) δ, ppm: 2.34 s (3H, CH_3), 2.39 s (3H, CH_3), 4.77 q (1H, C^2H, $^3J_{H-F}$ 8.8 Hz), 7.07-7.10 m ($2H_{arom.}$), 7.11 s (C^4H), 7.34 d ($2H_{arom.}$, ^3J 8.5 Hz), 7.38 d ($1H_{arom.}$, ^3J 8.4 Hz), 7.50 d ($2H_{arom.}$, ^3J 8.5 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz, measured in a mixture with **8n**) δ, ppm: 20.0 (CH_3), 21.2 (CH_3), 56.0 q (C^2, J_{C-F} 27.6 Hz), 120.1 q (C^3, J_{C-F} 1.1 Hz), 125.5 q (C^1, J_{C-F} 282.1 Hz), 127.3, 128.1 q (J_{C-F} 1.5 Hz), 128.5, 128.6, 130.6, 131.2 q (C^4, J_{C-F} 1.0 Hz), 131.9, 134.0, 134.3, 137.5, 138.7. ^{19}F NMR ($CDCl_3$, 376 MHz, measured in a mixture with **8n**) δ, ppm: -65.13 d (CF_3, J_{H-F} 8.8 Hz). MS (GC-MS, EI), m/z, ($I_{rel.}$, %): 402/404/406 (71/93/24) $[M]^+$, 387/389/391 (10/14/5), 323/325 (85/31), 308 (9), 288 (11), 254 (38), 239 (15), 229 (18), 211 (27), 203 (18), 125/127 (100/47), 108 (24), 101 (35), 95 (12), 77 (11). HRMS (MALDI-TOF): $C_{18}H_{16}BrClF_3$ found 403.0070 $[M+H]^+$; calcd. 403.0071.

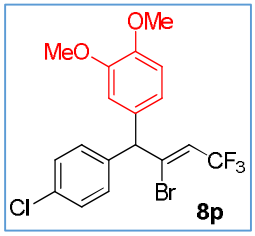
(*Z*)-3-Bromo-4-(4-chloropenyl)-1,1,1-trifluoro-4-(2,4,5-trimethylphenyl)but-2-ene (8o) and (*Z*)-3-bromo-4-(4-chlorophenyl)-1,1,1-trifluoro-2-(2,4,5-trimethylphenyl)but-2-ene (9p): The reaction scale is 60 mg (0.2 mmol) alcohol **2d** and 24 mg (0.2 mmol) pseudocumene, isolated amount is 68 mg a mixture of **8o** and **9p** (total yield 85%, ratio **8o** : **9p** = 1.1:1). Compound **8o**: Colorless solid, mp 106-108°C (MeOH). ^{1}H NMR ($CDCl_3$, 400 MHz, measured in a mixture with **9p**) δ, ppm: 2.18 s (3H, CH_3), 2.19 s (3H, CH_3), 2.22 s (3H, CH_3), 5.23 m (1H, C^4H), 5.81 qd (1H, C^2H, $^3J_{H-F}$ 7.2 Hz, ^4J 1.2 Hz), 6.64 s ($1H_{arom.}$), 6.99 s ($1H_{arom.}$), 7.10 d ($2H_{arom.}$, ^3J 8.5 Hz), 7.34 d ($2H_{arom.}$, ^3J 8.5 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz, measured in a mixture with **9p**) δ, ppm: 19.0 (CH_3), 19.4 (CH_3), 19.6 (CH_3), 59.1 (C^4), 122.2 q (C^1, J_{C-F} 270.9 Hz), 122.7 q (C^2, J_{C-F} 36.0 Hz), 129.2, 129.6, 130.8, 132.6, 133.7, 133.8, 134.6, 134.7, 136.4, 137.5, 139.6 q (C^3, J_{C-F} 6.1 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz, measured in a mixture with **9p**) δ, ppm: -59.14 dd (CF_3, J_{H-F} 7.2 Hz, J_{H-F} 2.1 Hz). MS (GC-MS, EI), m/z, ($I_{rel.}$, %): 416/418/420 $[M]^+$ (51/67/17), 337/339 (28/9), 322 (7), 287 (8), 243/245 (100/35), 115 (12), 217 (28), 208 (16), 193 (24), 178 (11), 159 (8), 141 (15), 125/127 (100/35), 119 (21), 115 (15), 101 (15), 91 (14), 77 (13), 65 (5), 41 (6). HRMS (MALDI-TOF): $C_{19}H_{18}BrClF_3$ found 417.0225 $[M+H]^+$; calcd. 417.0227. Compound **9p**: ^{1}H NMR ($CDCl_3$, 400 MHz, measured in a mixture with **8o**) δ, ppm: 2.24 s (3H, CH_3), 2.26 s (3H, CH_3), 2.35 s (3H, CH_3), 4.75 q (1H, C^2H, $^3J_{H-F}$ 8.9 Hz), 7.03 s ($1H_{arom.}$), 7.11 (1H, C^4H), 7.23 s ($1H_{arom.}$), 7.34 d ($2H_{arom.}$, ^3J 8.5 Hz), 7.52 d ($2H_{arom.}$, ^3J 8.5 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz, measured in a mixture with **8o**) δ, ppm: 19.4 (CH_3), 19.5 (CH_3), 19.7 (CH_3), 56.1 q (C^2, J_{C-}



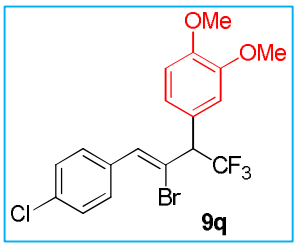


$_F$ 26.4 Hz), 120.2 q (C^3, J_{C-F} 1.1 Hz), 124.0 q (C^1, J_{C-F} 279.9 Hz), 128.6, 129.2, 130.6, 130.9, 131.0 q (C^4, J_{C-F} 1.1 Hz), 132.4, 134.0, 134.3, 134.7, 134.8, 137.3. ^{19}F NMR ($CDCl_3$, 376 MHz, measured in a mixture with **8o**) δ, ppm: -65.03 d (CF_3, J_{H-F} 8.9 Hz). MS (GC-MS, EI), m/z, ($I_{rel.}$, %): 416/418/420 $[M]^+$ (26/31/8), 401/403/405 (4/5/1), 337/339 (19/6), 268 (14), 253 (8), 229 (6), 217 (13), 203 (6), 141 (6), 125/127 (100/33), 119 (14), 108 (11), 101 (11), 91 (6). HRMS (MALDI-TOF): $C_{19}H_{18}BrClF_3$ found 417.0225 $[M+H]^+$; calcd. 417.0227.

(*Z*)-3-Bromo-4-(4-chloropenyl)-1,1,1-trifluoro-4-(3,4-dimethoxyphenyl)but-2-ene

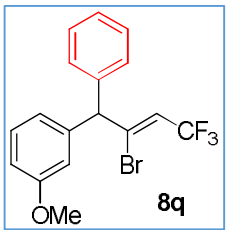


(8p) and (Z)-3-bromo-4-(4-chlorophenyl)-1,1,1-trifluoro-2-(3,4-dimethoxyphenyl)but-2-ene (9q): The reaction scale is 60 mg (0.2 mmol) alcohol **2d** and 28 mg (0.21 mmol) veratrole, isolated amount is 68 mg a mixture of **8p** and **9q** (total yield 85%, ratio **8p** : **9q** = 1.1:1). Compound **8p**: ^{1}H NMR ($CDCl_3$, 400 MHz, measured in a mixture with **9q**) δ, ppm: 3.83 s (3H, CH_3), 3.88 s (3H, CH_3), 5.12 m (1H, C^4H), 5.92 qd (1H, C^2H, $^3J_{H-F}$ 7.1 Hz, ^4J 1.2 Hz), 6.64-6.67 m ($2H_{arom.}$), 6.84 d ($1H_{arom.}$, ^3J 8.1 Hz), 7.12 d ($2H_{arom.}$, ^3J 8.4 Hz), 7.34 d ($2H_{arom.}$, ^3J 8.4 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz, measured in a mixture with **9q**) δ, ppm: 56.0 (CH_3), 56.1 (CH_3), 61.9 (C^4), 111.5, 112.3, 121.4, 122.1 q (C^1, J_{C-F} 271.1 Hz), 123.0 q (C^2, J_{C-F} 36.0 Hz), 129.2, 130.5, 131.1, 133.8, 137.9, 139.9 q (C^3, J_{C-F} 5.9 Hz), 148.9, 149.5. ^{19}F NMR ($CDCl_3$,



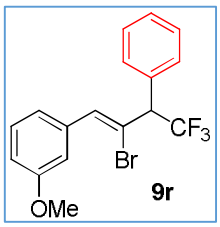
376 MHz, measured in a mixture with **9q**) δ, ppm: -59.18 dd (CF_3, J_{H-F} 7.1 Hz, J_{H-F} 2.0 Hz). MS (GC-MS, EI), m/z, ($I_{rel.}$, %): 434/436/438 $[M]^+$ (57/74/19), 355/357 (11/4), 320 (28), 285 (7), 261/263 (100/33), 217 (18), 182 (7), 165 (17), 152 (9), 138 (32), 107 (6), 88 (6), 79 (10), 51 (10). HRMS (MALDI-TOF): $C_{18}H_{16}O_2BrClF_3$ found 434.9971 $[M+H]^+$; calcd. 434.9969. Compound **9q**: ^{1}H NMR ($CDCl_3$, 400 MHz, measured in a mixture with **8p**) δ, ppm: 3.90 s (6H, CH_3), 4.47 q (1H, C^2H, $^3J_{H-F}$ 8.9 Hz), 6.89 d ($1H_{arom.}$, ^3J 8.4 Hz), 6.93 s ($1H_{arom.}$), 7.00 dd ($1H_{arom.}$, ^3J 8.3 Hz, ^4J 1.7 Hz), 7.15 s (1H, C^4H), 7.35 d ($1H_{arom.}$, ^3J 8.5 Hz), 7.53 d ($1H_{arom.}$, ^3J 8.5 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz, measured in a mixture with **8p**) δ, ppm: 56.0 (CH_3), 56.2 (CH_3), 60.4 q (C^2, J_{C-F} 27.9 Hz), 111.3, 112.5, 119.9 q (C^3, J_{C-F} 1.1 Hz), 122.1, 124.9, 125.1 q (C^1, J_{C-F} 281.8 Hz), 128.6, 130.6, 131.2 q (C^4, J_{C-F} 1.2 Hz), 133.9, 134.4, 149.2, 149.7. ^{19}F NMR ($CDCl_3$, 376 MHz, measured in a mixture with **8p**) δ, ppm: -65.55 d (CF_3, J_{H-F} 8.9 Hz). MS (GC-MS, EI), m/z, ($I_{rel.}$, %): 434/436/438 $[M]^+$ (80/100/30), 365/367/369 (7/10/2), 355/357 (12/4), 320 (23), 286 (24), 271 (11), 261 (12), 251 (8), 229 (7), 217 (15), 165 (12), 143 (15), 138 (51), 125 (12), 104 (8), 82 (10), 51 (5). HRMS (MALDI-TOF): $C_{18}H_{16}O_2BrClF_3$ found 434.9971 $[M+H]^+$; calcd. 434.9969.

(*Z*)-3-Bromo-1,1,1-trifluoro-4-(3-methoxyphenyl)-4-penylbut-2-



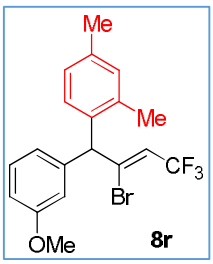
ene (8q) and (*Z*)-3-bromo-1,1,1-trifluoro-4-(3-methoxyphenyl)-3-

phenylbut-2-ene (9r): The reaction scale is 60 mg (0.2 mmol) alcohol **2e** and 748 mg (9.6 mmol) benzene at 20°C, isolated amount is 40 mg a mixture of **8q** and **9r** and 12 mg **9r** (total yield 70%, ratio **8q** : **9r** = 1:1.2). Compound **8q**: ^{1}H NMR ($CDCl_3$, 400 MHz, measured in a mixture with **9r**) δ, ppm: 3.79 s (3H, CH_3), 5.17 m (1H, C^4H), 5.93 qd (1H, C^2H, $^{3}J_{H\text{-}F}$ 7.2 Hz, ^{4}J 1.3 Hz), 6.71-6.72 m ($1H_{arom.}$), 6.78 d ($1H_{arom.}$, ^{3}J 7.7 Hz), 6.84 dd ($1H_{arom.}$, ^{3}J 8.1 Hz, ^{4}J 2.3 Hz), 7.18-7.19 m ($1H_{arom.}$), 7.27-7.38 m ($4H_{arom.}$), 7.40-7.43 m ($1H_{arom.}$). ^{13}C NMR ($CDCl_3$, 100 MHz, measured in a mixture with **9r**) δ, ppm: 55.4 (CH_3), 63.0 (C^4), 112.8, 115.4, 121.6, 122.2 q (C^1, $J_{C\text{-}F}$ 270.9 Hz), 123.0 q (C^2, $J_{C\text{-}F}$ 35.9 Hz), 127.9, 129.0, 129.2, 130.0, 139.1, 139.9 q (C^3, $J_{C\text{-}F}$ 6.0 Hz), 140.7, 160.1. ^{19}F NMR ($CDCl_3$, 376 MHz, measured in a mixture with **9r**) δ, ppm: -59.16 dd (CF_3, J 7.2 Hz, J 2.1 Hz). MS (GC-MS, EI), m/z, ($I_{rel.}$, %): 370/372 (90/82) $[M]^+$, 303 (10), 291 (100), 271 (10), 256 (7), 213 (50), 197 (30), 183 (92), 165 (30), 126 (20), 95 (10), 77 (20), 63 (12), 51 (10). HRMS (MALDI-TOF): $C_{17}H_{15}BrF_3O$ found 371.0253 $[M+H]^+$; calcd. 371.0253. Compound **9r**: Yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 3.83 s (3H, CH_3), 4.55 q (1H, C^2H, $^{3}J_{H\text{-}F}$ 8.9 Hz), 6.89 dd ($1H_{arom.}$, ^{3}J 8.3 Hz, ^{4}J 2.4 Hz), 7.15 d ($1H_{arom.}$, ^{3}J 7.7 Hz), 7.18 d ($1H_{arom.}$, ^{4}J 2.0 Hz), 7.21 s (1H, C^4H), 7.29 t ($1H_{arom.}$, ^{3}J 8.0 Hz), 7.39-7.47 m ($5H_{arom.}$). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 55.5 (CH_3), 60.9 q (C^2, $J_{C\text{-}F}$ 27.8 Hz), 114.4, 114.5, 118.9 q (C^3, $J_{C\text{-}F}$ 1.5 Hz), 121.9, 125.1 q (C^1, $J_{C\text{-}F}$ 281.9 Hz), 128.9, 129.4, 129.5 (2C), 132.6 q (C^4, $J_{C\text{-}F}$ 1.3 Hz), 132.9, 136.7, 159.5. ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: -65.39 d (CF_3, J 8.9 Hz). MS (GC-MS, EI), m/z, ($I_{rel.}$, %): 370/372 (40/42) $[M]^+$, 291 (60), 213 (10), 183 (100), 133 (10), 111 (11), 89 (12), 76 (8). HRMS (MALDI-TOF): $C_{17}H_{15}BrF_3O$ found 371.0253 $[M+H]^+$; calcd. 371.0253.

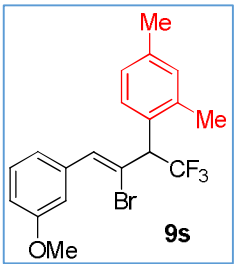


9r

(*Z*)-3-Bromo-1,1,1-trifluoro-4-(3-methoxypenyl)-4-(2,4-dimethylphenyl)but-2-ene (8r) and (*Z*)-3-bromo-1,1,1-trifluoro-4-(3-methoxyphenyl)-2-(2,4-dimethylphenyl)but-3-ene (9s): The reaction scale is 60 mg (0.2 mmol) alcohol **2e** and 22 mg (0.2 mmol) *meta*-xylene at 20°C, isolated amount is 68 mg a mixture of **8r** and **9s** (total yield 85%, ratio **8r**:**9s** = 1:2.8). Compound **8r**: ^{1}H NMR ($CDCl_3$, 400 MHz, measured in a mixture with **9s**) δ, ppm: 2.24 s (3H, CH_3), 2.32 s (3H, CH_3), 3.79 s (3H, OCH_3), 5.25 m (1H, C^4H), 5.84 qd (1H, C^2H, $^{3}J_{H\text{-}F}$ 7.3 Hz, ^{4}J 1.2 Hz), 6.69 d ($1H_{arom.}$, ^{4}J 1.9 Hz), 6.75 d ($1H_{arom.}$, ^{3}J 7.6 Hz), 6.84 dd ($1H_{arom.}$, ^{3}J 8.2 Hz, ^{4}J 2.2 Hz), 6.87-6.89 m ($1H_{arom.}$), 7.00 d ($1H_{arom.}$, ^{3}J 7.9 Hz), 7.04 m ($1H_{arom.}$), 7.09-7.14 m ($1H_{arom.}$). ^{13}C NMR ($CDCl_3$, 100 MHz, measured in a mixture with **9s**) δ, ppm: 19.9 (CH_3), 21.2 (CH_3), 55.5 (OCH_3), 59.7 (C^4), 112.8, 115.6, 121.9, 122.3 q (C^1, $J_{C\text{-}F}$ 270.8 Hz), 122.6 q (C^2, $J_{C\text{-}F}$ 36.0 Hz), 127.1, 127.3, 128.4, 131.9, 134.8, 136.6, 137.6, 139.9 q (C^3, $J_{C\text{-}F}$ 6.7 Hz), 140.3, 159.5. ^{19}F NMR ($CDCl_3$, 376 MHz, measured in a mixture with



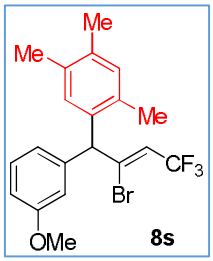
8r

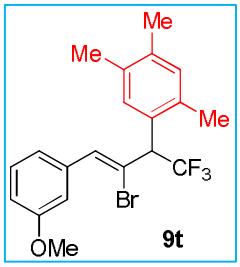


9s

9s) δ, ppm: -59.12 dd (CF_3, J_{H-F} 7.3 Hz, J_{H-F} 2.1 Hz). MS (GC-MS, EI), m/z, ($I_{rel.}$, %): 398/400 (98/96) $[M]^+$, 319 (100), 287 (7), 249 (9), 225 (46), 211 (74), 189 (15), 179 (13), 165 (12), 142 (18), 121 (61), 105 (29), 89 (12), 77 (28), 51 (5). HRMS (MALDI-TOF): $C_{19}H_{19}BrF_3O$ found 399.0565 $[M+H]^+$; calcd. 399.0566. Compound **9s**: ^{1}H NMR ($CDCl_3$, 400 MHz, measured in a mixture with **8r**) δ, ppm: 2.34 s (3H, CH_3), 2.40 s (3H, CH_3), 3.82 s (3H, OCH_3), 4.79 q (1H, C^2H, $^3J_{H-F}$ 8.8 Hz), 6.87-6.89 m (1$H_{arom.}$), 7.08-7.16 m (4H, C^4H, 3$H_{arom.}$), 7.25-7.30 m (2$H_{arom.}$), 7.42 d (1$H_{arom.}$, ^3J 8.2 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz, measured in a mixture with **8r**) δ, ppm: 19.6 (CH_3), 31.0 (CH_3), 55.3 (OCH_3), 56.1 q (C^2, J_{C-F} 27.9 Hz), 114.3, 114.4, 119.3 q (C^3, J_{C-F} 1.5 Hz), 121.9, 125.5 q (C^1, J_{C-F} 282.0 Hz), 128.2 q (J_{C-F} 1.5 Hz), 128.7, 129.3, 130.0, 131.9, 132.2 q (C^4, J_{C-F} 1.3 Hz), 136.8, 137.5, 138.6, 160.1. ^{19}F NMR ($CDCl_3$, 376 MHz, measured in a mixture with **8r**) δ, ppm: -65.13 d (CF_3, J_{H-F} 8.8 Hz). MS (GC-MS, EI), m/z, ($I_{rel.}$, %): 398/400 (64/62) $[M]^+$, 319 (60), 250 (10), 235 (9), 211 (55), 191 (17), 165 (5), 142 (12), 121 (100), 101 (11), 91 (15), 77 (12). HRMS (MALDI-TOF): $C_{19}H_{19}BrF_3O$ found 399.0565 $[M+H]^+$; calcd. 399.0566.

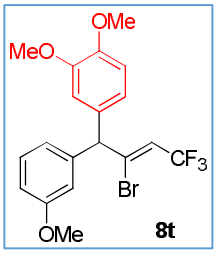
(*Z*)-3-Bromo-1,1,1-trifluoro-4-(3-methoxyphenyl)-4-(2,4,5-trimethylpenyl)but-2-ene (8s) and (*Z*)-3-bromo-1,1,1-trifluoro-4-(3-methoxyphenyl)-2-(2,4,5-trimethylphenyl)but-2-ene (9t): The reaction scale is 60 mg (0.2 mmol) alcohol **2e** and 26 mg (0.2 mmol) pseudocumene at 20°C, isolated amount is 52 mg a mixture of **8s** and **9t** (total yield 65%, ratio **8s**:**9t** = 1:3.4). Compound **8s**: ^{1}H NMR ($CDCl_3$, 400 MHz, measured in a mixture with **9t**) δ, ppm: 2.19 s (3H, CH_3), 2.20 s (3H, CH_3), 2.22 s (3H, CH_3), 3.80 s (3H, OCH_3), 5.23 m (1H, C^4H), 5.84 q (1H, C^2H, $^3J_{H-F}$ 7.2 Hz), 6.70 s (1$H_{arom.}$), 6.72 s (1$H_{arom.}$), 6.75 d (1$H_{arom.}$, ^3J 7.8 Hz), 6.85 dd (1$H_{arom.}$, ^3J 8.3 Hz, ^4J 2.4 Hz), 6.98 s (1$H_{arom.}$), 7.27-7.31 m (1$H_{arom.}$). ^{13}C NMR ($CDCl_3$, 100 MHz, measured in a mixture with **9t**) δ, ppm: 19.1 (CH_3), 19.4 (CH_3), 19.6 (CH_3), 55.3 (OCH_3), 59.7 (C^4), 112.6, 115.7, 122.3 q (C^1, J_{C-F} 271.0 Hz), 122.5 q (C^2, J_{C-F} 36.1 Hz), 127.0, 129.6, 130.0, 132.5, 133.9, 134.4, 135.0, 136.1, 140.0 q (C^3, J_{C-F} 6.1 Hz), 140.4, 160.1. ^{19}F NMR ($CDCl_3$, 376 MHz, measured in a mixture with **9t**) δ, ppm: -59.07 dd (CF_3, J_{H-F} 7.2 Hz, J_{H-F} 2.1 Hz). MS (GC-MS, EI), m/z, ($I_{rel.}$, %): 412/414 $[M]^+$ (100/96), 381/383 (5), 333 (86), 318 (10), 301 (5), 264 (15), 249 (13), 225 (60), 213 (53), 189 (5), 156 (7), 132 (7), 121 (95), 91 (20), 77 (7), 63 (5). HRMS (MALDI-TOF): $C_{20}H_{21}BrF_3O$ found 413.0723 $[M+H]^+$; calcd. 413.0722. Compound **9t**: ^{1}H NMR ($CDCl_3$, 400 MHz, measured in a mixture with **8s**) δ, ppm: 2.24 s (3H, CH_3), 2.26 s (3H, CH_3), 2.36 s (3H, CH_3), 3.82 s (3H, OCH_3), 4.75 q (1H, C^2H, $^3J_{H-F}$ 8.9 Hz), 6.88 dd (1$H_{arom.}$, ^3J 8.3 Hz, ^4J 2.2 Hz), 7.02 s (1$H_{arom.}$), 7.14 d (1$H_{arom.}$, ^3J 8.0 Hz), 7.15 s (1H, C^4H), 7.17 s (1$H_{arom.}$), 7.24 s (1$H_{arom.}$), 7.14 t (1$H_{arom.}$, ^3J 8.0 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz, measured in a



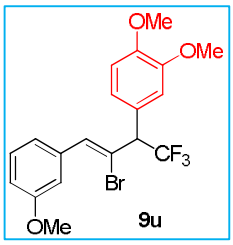


mixture with **8s**) δ, ppm: 19.3 (CH_3), 19.4 (CH_3), 19.6 (CH_3), 55.3 (OCH_3), 55.9 q (C^2, J_{C-F} 27.5 Hz), 114.1, 114.3, 119.3 q (C^3, J_{C-F} 1.6 Hz), 121.7, 125.4 q (C^1, J_{C-F} 282.0 Hz), 128.6, 129.1 q (J_{C-F} 1.2 Hz), 129.2, 131.8 q (C^4, J_{C-F} 1.5 Hz), 132.2, 134.5, 134.7, 136.7, 137.1, 159.3. ^{19}F NMR ($CDCl_3$, 376 MHz, measured in a mixture with **8s**) δ, ppm: -65.05 d (CF_3, J_{H-F} 8.9 Hz). MS (GC-MS, EI), m/z, ($I_{rel.}$, %): 412/414 $[M]^+$ (95/100), 381/383 (3), 333 (75), 301 (6), 263 (10), 239 (45), 225 (50), 213 (27), 209 (12), 189 (10), 165 (7), 141 (10), 121 (72), 91 (15), 77 (10), 63 (5), 41 (5). HRMS (MALDI-TOF): $C_{20}H_{21}BrF_3O$ found 413.0723 $[M+H]^+$; calcd. 413.0722.

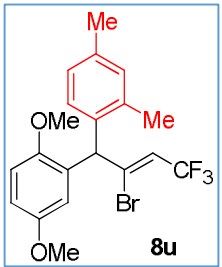
(*Z*)-3-Bromo-1,1,1-trifluoro-4-(3-methoxypenyl)-4-(3,4-dimethoxyphenyl)but-2-ene



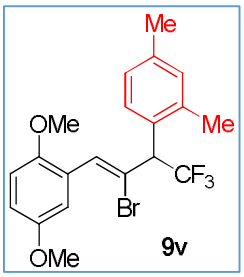
(8t) and (*Z*)-3-bromo-1,1,1-trifluoro-4-(3-methoxyphenyl)-2-(3,4-dimethoxyphenyl)but-2-ene (9u): The reaction scale is 60 mg (0.2 mmol) alcohol **2e** and 30 mg (0.2 mmol) veratrole at 20°C, isolated amount is 52 mg a mixture of **8t** and **9u** (total yield 60%, ratio **8t**:**9u** = 1.6:1). Compound **8t**: ^1H NMR ($CDCl_3$, 400 MHz, measured in a mixture with **9u**) δ, ppm: 3.79 s (3H, CH_3), 3.83 s (3H, CH_3), 3.88 s (3H, CH_3), 5.11 m (1H, C^4H), 5.93 qd (1H, C^2H, $^3J_{H-F}$ 7.3 Hz, ^4J 1.2 Hz), 6.68-6.71 m ($3H_{arom.}$), 6.78 d ($1H_{arom.}$, ^3J 7.7 Hz), 6.83-6.85 m ($2H_{arom.}$), 7.27-7.31 m ($1H_{arom.}$). ^{13}C NMR ($CDCl_3$, 100 MHz, measured in a mixture with **9u**) δ, ppm: 55.4 (CH_3), 56.0 (CH_3), 56.1 (CH_3), 62.6 (C^4), 111.4, 112.5, 112.8, 115.4, 121.4, 121.5, 122.3 q (C^1, J_{C-F} 270.8 Hz), 122.7 q (C^2, J_{C-F} 36.0 Hz), 130.0, 136.7, 140.2 q (C^3, J_{C-F} 6.2 Hz), 140.9, 148.7, 149.3, 160.1. ^{19}F NMR ($CDCl_3$, 376 MHz, measured in a mixture with **9u**) δ, ppm: -59.13 dd (CF_3, J_{H-F} 7.3 Hz, J_{H-F} 2.0 Hz). MS (GC-MS, EI), m/z, ($I_{rel.}$, %): 430/432 $[M]^+$ (100/93), 351 (25), 320 (8), 257 (100), 243 (28), 226 (14), 213 (42), 165 (7), 138 (9), 77 (6). HRMS (MALDI-TOF): $C_{19}H_{19}BrF_3O_2$ found 431.0464 $[M+H]^+$; calcd. 431.0464. Compound **9u**: ^1H NMR ($CDCl_3$, 400 MHz, measured in a mixture with **8t**) δ, ppm: 3.83 s (3H, CH_3), 3.90 s (6H, CH_3), 4.48 q (1H, C^2H, $^3J_{H-F}$ 8.9 Hz), 6.88-6.90 m ($2H_{arom.}$), 6.95 s ($1H_{arom.}$), 7.02 dd ($1H_{arom.}$, ^3J 8.3 Hz, ^4J 1.6 Hz), 7.14 d ($1H_{arom.}$, ^3J 7.7 Hz), 7.18-7.19 m (2H, C^4H, $H_{arom.}$), 7.27-7.31 m ($1H_{arom.}$). ^{13}C NMR ($CDCl_3$, 100 MHz, measured in a mixture with **8t**) δ, ppm: 55.5 (CH_3), 56.0 (CH_3), 56.2 (CH_3), 60.5 q (C^2, J_{C-F} 27.9 Hz), 111.3, 112.5, 114.4, 114.5, 119.2 q (C^3, J_{C-F} 1.5 Hz), 121.9, 122.1, 125.2 q (C^1, J_{C-F} 281.7 Hz), 129.4, 130.4, 132.3 q (C^4, J_{C-F} 1.4 Hz), 137.6, 149.2, 149.6, 159.5. ^{19}F NMR ($CDCl_3$, 376 MHz, measured in a mixture with **8t**) δ, ppm: -65.55 d (CF_3, J_{H-F} 8.9 Hz). MS (GC-MS, EI), m/z, ($I_{rel.}$, %): 430/432 $[M]^+$ (100/99), 415/417 (5/4), 351 (28), 320 (7), 282 (11), 267 (10), 243 (62), 225 (8), 213 (54), 175 (10), 141 (12), 119 (5), 89 (6), 76 (5). HRMS (MALDI-TOF): $C_{19}H_{19}BrF_3O_2$ found 431.0464 $[M+H]^+$; calcd. 431.0464.



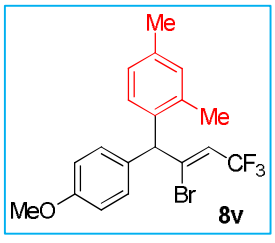
(*Z*)-3-Bromo-1,1,1-trifluoro-4-(2,5-dimethoxypenyl)-4-(2,4-dimetylphenyl)but-2-ene (8u) and (*Z*)-3-bromo-1,1,1-trifluoro-4-(2,5-

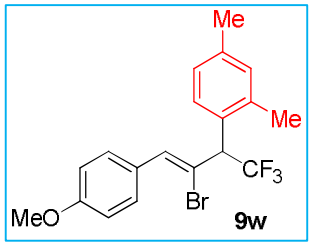


dimethoxyphenyl)-2-(2,4-dimethylphenyl)but-3-ene (9v): The reaction scale is 60 mg (0.18 mmol) alcohol **2g** and 22 mg (0.2 mmol) *meta*-xylene, isolated amount is 34 mg **8u** and 14 mg a mixture of **8u** and **9v** (total yield 62%, ratio **8u** : **9v** = 3.8:1). Compound **8u**: Colorless solid, mp 107-109°C (MeOH). ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 2.19 s (3H, CH_3), 2.31 s (3H, CH_3), 3.71 s (3H, OCH_3), 3.76 s (3H, OCH_3), 5.61 m (1H, C^4H), 5.80 qd (1H, C^2H, $^3J_{H-F}$ 7.2 Hz, ^4J 1.0 Hz), 6.49 d (1$H_{arom.}$, ^4J 2.9 Hz), 6.80 dd (1$H_{arom.}$, ^3J 8.9 Hz, ^4J 2.9 Hz), 6.84 d (1$H_{arom.}$, ^3J 8.9 Hz), 6.92 d (1$H_{arom.}$, ^3J 7.8 Hz), 6.98 d (1$H_{arom.}$, ^3J 8.1 Hz), 7.02 s (1$H_{arom.}$). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 19.4 (CH_3), 21.1 (CH_3), 52.8 (C^4), 55.7 (OCH_3), 56.4 (OCH_3), 112.0, 112.5, 116.5, 121.4 q (C^2, J_{C-F} 35.8 Hz), 122.4 q (C^1, J_{C-F} 270.7 Hz), 127.0, 128.1, 129.1, 131.9, 134.4, 136.8, 137.3, 139.9 q (C^3, J_{C-F} 6.0 Hz), 151.5, 153.6. ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: -59.00 dd (CF_3, J_{H-F} 7.2 Hz, J_{H-F} 2.1 Hz). MS (GC-MS, EI), m/z, ($I_{rel.}$, %): 428/430 (57/54) $[M]^+$, 349 (8), 333 (11), 317 (10), 225 (6), 211 (33), 149 (6), 138 (11), 119 (100), 105 (10), 91 (9), 77 (13). HRMS (MALDI-TOF): $C_{20}H_{21}BrF_3O_2$ found 429.0670 $[M+H]^+$; calcd. 429.0672. Compound **9v**: ^{1}H NMR ($CDCl_3$, 400 MHz, measured in a mixture with **8u**) δ, ppm: 2.33 s (3H, CH_3), 2.40 s (3H, CH_3), 3.77 s (3H, OCH_3), 3.79 s (3H, OCH_3), 4.79 q (1H, C^2H, $^3J_{H-F}$ 8.9 Hz), 6.82-6.86 m (2$H_{arom.}$), 7.08 d (2$H_{arom.}$, ^3J 8.5 Hz), 7.28 d (1$H_{arom.}$, ^4J 2.8 Hz), 7.30 s (1H, C^4H), 7.45 d (1$H_{arom.}$, ^3J 7.8 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz, measured in a mixture with **8u**) δ, ppm: 19.9 (CH_3), 21.2 (CH_3), 55.9 q (C^2, J_{C-F} 27.6 Hz), 56.0 (OCH_3), 56.6 (OCH_3), 113.9, 114.9, 115.5, 119.2, 119.7 q (C^3, J_{C-F} 1.6 Hz), 125.5 q (C^1, J_{C-F} 282.1 Hz), 125.6, 127.2, 128.4 (C^4), 128.6, 131.8, 137.5, 138.5, 151.7, 153.1. ^{19}F NMR ($CDCl_3$, 376 MHz, measured in a mixture with **8u**) δ, ppm: -65.27 d (CF_3, J_{H-F} 8.9 Hz). MS (GC-MS, EI), m/z, ($I_{rel.}$, %): 428/430 (100/100) $[M]^+$, 349 (12), 314 (9), 280 (21), 265 (14), 211 (24), 187 (33), 167 (11), 151 (43), 140 (20), 121 (19), 105 (11), 91 (16), 77 (15), 65 (10), 51 (6). HRMS (MALDI-TOF): $C_{20}H_{21}BrF_3O_2$ found 429.0670 $[M+H]^+$; calcd. 429.0672.



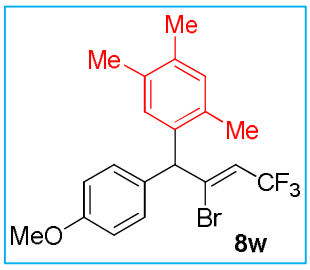
(*Z*)-3-Bromo-1,1,1-trifluoro-4-(4-methoxypenyl)-4-(2,4-dimethylphenyl)but-2-ene (8v) and (*Z*)-3-bromo-1,1,1-trifluoro-4-(4-methoxyphenyl)-2-(2,4-dimethylphenyl)but-2-ene (9w): The reaction scale is 60 mg (0.2 mmol) alcohol **2f** and 24 mg (0.22 mmol) *meta*-xylene, isolated amount is 18 mg **8v** and 18 mg a mixture of **8v** and **9w** (total yield 47%, ratio **8v** : **9w** = 1.3:1). Compound **8v**: Pale yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 2.22 s (3H, CH_3), 2.31 s (3H, CH_3), 3.81 s (3H, CH_3O), 5.22 m (1H, C^4H), 5.80 qd (1H, C^2H, $^3J_{H-F}$ 7.2 Hz, ^4J 1.3 Hz), 6.85-6.89 m (3$H_{arom.}$), 7.00 d (1$H_{arom.}$, ^3J 8.2 Hz), 7.02 s (1$H_{arom.}$), 7.05 d (2$H_{arom.}$, ^3J 8.7 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 19.6 (CH_3), 21.1 (CH_3), 55.4 (CH_3O), 59.0 (C^4), 114.4, 122.3 q (C^1, J_{C-F} 270.8 Hz),



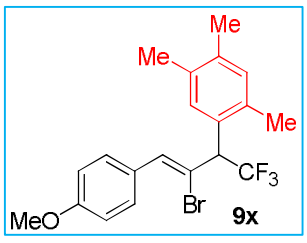


122.4 q (C^2, J_{C-F} 35.9 Hz), 127.0, 128.3, 130.5, 130.8, 131.9, 135.2, 136.5, 137.4, 140.6 q (C^3, J_{C-F} 6.1 Hz), 159.1. ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: -59.07 dd (CF_3, J_{H-F} 7.2 Hz, J_{H-F} 2.2 Hz). MS (GC-MS, EI), m/z, ($I_{rel.}$, %): 398/400 $[M]^+$ (48/46), 319 (42), 250 (5), 225 (100), 211 (23), 195 (6), 142 (10), 119 (9), 105 (8), 77 (6). HRMS (MALDI-TOF): $C_{19}H_{19}BrF_3O$ found 399.0566 $[M+H]^+$; calcd. 399.0566. Compound **9w**: ^{1}H NMR ($CDCl_3$, 400 MHz, measured in a mixture with **8v**) δ, ppm: 2.33 s (3H, CH_3), 2.39 s (3H, CH_3), 3.83 s (3H, CH_3O), 4.76 q (1H, C^2H, $^3J_{H-F}$ 8.9 Hz), 6.89 d ($2H_{arom.}$, ^3J 8.8 Hz), 7.06-7.08 m (3H, C^4H, $2H_{arom.}$), 7.41 d ($1H_{arom.}$, ^3J 8.1 Hz), 7.57 d ($2H_{arom.}$, ^3J 8.7 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz, measured in a mixture with **8v**) δ, ppm: 20.0 (CH_3), 21.2 (CH_3), 55.4 (CH_3O), 56.1 q (C^2, J_{C-F} 27.4 Hz), 113.7, 117.1 (C^3), 125.6 q (C^1, J_{C-F} 282.8 Hz), 127.2, 127.9, 128.2, 128.9, 130.8, 131.8 (C^4), 131.8, 137.4, 138.5, 159.8. ^{19}F NMR ($CDCl_3$, 376 MHz, measured in a mixture with **8v**) δ, ppm: -65.13 d (CF_3, J_{H-F} 8.9 Hz). MS (GC-MS, EI), m/z, ($I_{rel.}$, %): 398/400 $[M]^+$ (73/74), 319 (20), 250 (22), 223 (26), 211 (40), 191 (14), 142 (10), 121 (100), 109 (17), 89 (8), 77 (7). HRMS (MALDI-TOF): $C_{19}H_{19}BrF_3O$ found 399.0566 $[M+H]^+$; calcd. 399.0566.

(*Z*)-3-Bromo-1,1,1-trifluoro-4-(4-methoxypenyl)-4-(2,4,5-trimethylphenyl)but-2-ene (8w) and (*Z*)-3-bromo-1,1,1-trifluoro-4-(4-methoxyphenyl)-2-(2,4,5-trimethylphenyl)-but-2-ene (9x): The reaction scale is 60 mg (0.2 mmol) alcohol **2f** and 26 mg (0.22 mmol) pseudocumene, isolated amount is 22 mg a mixture of **8w** and **9x** (total yield 28%, ratio **8w** : **9x** = 1:8). Compound **8w**: ^{1}H NMR ($CDCl_3$, 400 MHz, measured in a mixture with **9x**) δ, ppm: 2.18 s (3H, CH_3), 2.19 s (3H, CH_3), 2.22 s (3H, CH_3), 3.81 s (3H, CH_3), 5.19 m (1H, C^4H), 5.81 dq (1H, C^2H, $^3J_{H-F}$ 7.3 Hz, ^4J 1.3 Hz), 6.07 s ($1H_{arom.}$), 6.87-6.92 m ($2H_{arom.}$), 6.97 s ($1H_{arom.}$), 7.05 d ($2H_{arom.}$, ^3J 8.6 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz, measured in a mixture with **9x**) δ, ppm: 19.0 (CH_3), 19.6 (CH_3), 22.0 (CH_3), 55.4 (CH_3), 59.0 (C^4), 114.3, 114.4, 122.3 q (C^2, J_{C-F} 35.9 Hz), 122.4 q (C^1, J_{C-F} 270.7 Hz), 129.4, 129.6, 130.5, 131.5, 132.5, 133.8, 134.4, 135.4, 136.0, 159.0. ^{19}F NMR ($CDCl_3$, 376 MHz, measured in a mixture with **9x**) δ, ppm: -59.03 dd (CF_3, J_{H-F} 7.3 Hz, J_{H-F} 2.2 Hz). MS (GC-MS, EI), m/z, ($I_{rel.}$, %): 412/414 $[M]^+$ (47/46), 333 (35), 264 (6), 239 (100), 225 (16), 213 (10), 156 (8), 121 (11), 91 (5). HRMS (MALDI-TOF): $C_{20}H_{21}BrF_3O$ found 413.0720 $[M+H]^+$; calcd. 413.0722. Compound **9w**: ^{1}H NMR ($CDCl_3$, 400 MHz, measured in a mixture with **8w**) δ, ppm: 2.24 s (3H, CH_3), 2.25 s (3H, CH_3), 2.35 s (3H, CH_3), 3.83 s (3H, CH_3), 4.73 q (1H, C^2H, $^3J_{H-F}$ 8.9 Hz), 6.90 d ($2H_{arom.}$, ^3J 8.9 Hz), 7.01 s ($1H_{arom.}$), 7.09 (1H, C^4H), 7.24 s ($1H_{arom.}$), 7.58 d ($2H_{arom.}$, ^3J 8.7 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz, measured in a mixture with **8w**) δ, ppm: 19.4 (CH_3), 19.5 (CH_3), 19.7 (CH_3), 55.4 (CH_3), 56.1 q (C^2, J_{C-F} 27.4

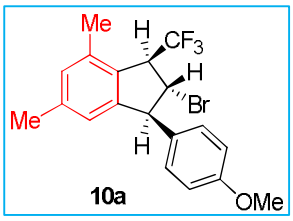


8w

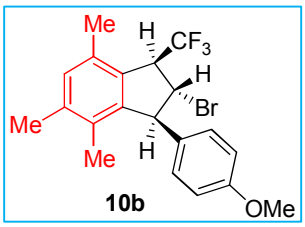


9x

Hz), 113.7, 117.2 q (C^3, J_{C-F} 1.5 Hz), 125.7 q (C^1, J_{C-F} 282.7 Hz), 127.9, 129.0, 129.3 q (J_{C-F} 1.1 Hz), 130.8, 131.6 q (C^4, J_{C-F} 1.1 Hz), 132.3, 134.6, 134.8, 137.1, 159.7. ^{19}F NMR ($CDCl_3$, 376 MHz, measured in a mixture with **8w**) δ, ppm: -65.04 d (CF_3, *J* 8.9 Hz). MS (GC-MS, EI), m/z, ($I_{rel.}$, %): 412/414 $[M]^+$ (31/35), 333 (16), 264 (12), 249 (8), 225 (26), 132 (9), 121 (100), 91 (6), 77 (5). HRMS (MALDI-TOF): $C_{20}H_{21}BrF_3O$ found 413.0720 $[M+H]^+$; calcd. 413.0722.



(*1SR,2RS,3SR*)-2-Bromo-1-(trifluoromethyl)-3-(4-methoxypenyl)-5,7-dimethylindane (10a): Pale yellow oil. The reaction scale is 60 mg (0.2 mmol) alcohol **2f** and 24 mg (0.22 mmol) *meta*-xylene, isolated amount is 14 mg **10a** (yield 18%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 2.31 s (3H, CH_3), 2.36 s (3H, CH_3), 3.80 s (3H, CH_3O), 4.29 qd (1H, C^1H, ^3J 3.1 Hz, $^3J_{H-F}$ 8.8 Hz,), 4.51 t (1H, C^2H, ^3J 3.6 Hz), 4.76 s (1H, C^3H, ^3J 3.7 Hz), 6.76 s (1H, C^4H), 6.86 d ($2H_{arom.}$, ^3J 8.6 Hz), 7.01 s (1H, C^6H), 7.10 d ($2H_{arom.}$, ^3J 8.6 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 20.2 q (CH_3, J_{C-F} 3.8 Hz), 21.3 (CH_3), 52.7 q (C^2, J_{C-F} 2.0 Hz), 55.4 (CH_3O), 59.6 q (C^1, J_{C-F} 28.5 Hz), 61.7 (C^3), 114.2, 124.1, 126.4 q (CF_3, J_{C-F} 281.1 Hz), 129.4, 130.2 q (J_{C-F} 1.7 Hz), 131.5, 133.8, 136.0, 139.8, 144.5, 159.0. ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: -66.56 dd (CF_3, *J* 8.8 Hz, *J* 0.8 Hz). MS (GC-MS, EI), m/z, ($I_{rel.}$, %): 398/400 $[M]^+$ (30/29), 319 (100), 303 (8), 249 (16), 235 (9), 213 (39), 191 (6), 159 (9), 125 (10), 101 (6), 77 (4). HRMS (MALDI-TOF): $C_{19}H_{19}BrF_3O$ found 399.0565 $[M+H]^+$; calcd. 399.0566.



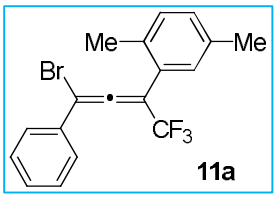
(*1SR,2RS,3SR*)-2-Bromo-1-(trifluoromethyl)-3-(4-methoxypenyl)-4,5,7-trimethylindane (10b): Colorless solid, mp 110-112°C (MeOH). The reaction scale is 60 mg (0.2 mmol) alcohol **2f** and 26 mg (0.22 mmol) pseudocumene, isolated amount is 32 mg **10b** (yield 40%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 1.89 s (3H, CH_3), 2.28 s (3H, CH_3), 2.33 s (3H, CH_3), 3.79 s (3H, CH_3O), 4.24 q (1H, C^1H, $^3J_{H-F}$ 9.3 Hz,), 4.62 s (1H, C^2H), 4.90 s (1H, C^3H), 6.81 d ($2H_{arom.}$, ^3J 8.7 Hz), 6.99 d ($2H_{arom.}$, ^3J 8.5 Hz), 7.06 s (1H, C^6H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 16.1 (CH_3), 19.7 q (CH_3, J_{C-F} 3.4 Hz), 19.8 (CH_3), 53.3 q (C^2, J_{C-F} 1.9 Hz), 55.3 (CH_3O), 60.2 q (C^1, J_{C-F} 28.6 Hz), 61.7 (C^3), 114.0, 126.2 q (CF_3, J_{C-F} 281.7 Hz), 129.0, 130.6 q (J_{C-F} 1.6 Hz), 131.6, 132.5, 133.0, 133.4, 138.7, 142.0, 158.7. ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: -66.35 d (CF_3, J_{H-F} 9.3 Hz). MS (GC-MS, EI), m/z, ($I_{rel.}$, %): 412/414 $[M]^+$ (58/60), 333 (94), 318 (11), 264 (19), 249 (15), 225 (100), 213 (31), 166 (12), 141 (6), 124 (13), 89 (6). HRMS (MALDI-TOF): $C_{20}H_{21}BrF_3O$ found 413.0723 $[M+H]^+$; calcd. 413.0722.

General procedure for synthesis of allenes 11a-g and 12a-c.

Potassium hydroxide (0.15 mmol) was added to a stirred solution of mono or dibromoalkene **5**, **8** (0.05 mmol) in ethanol (1 ml) at RT. Reaction mixture was magnetically

stirred for 24 h, then poured into water (30 mL) and extracted with ether (2×30 mL). The extracts were combined, washed with water and dried over Na_2SO_4. The solvent was distilled off under reduced pressure, crude mixture was purified by preparative TLC on silica gel using petroleum ether or petroleum ether-EtOAc mixture (95:5) as an eluent.

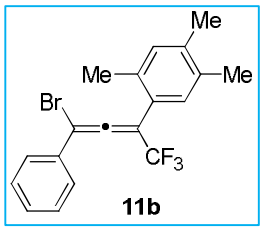
4-Bromo-1,1,1-trifluoro-2-(2,5-dimethylphenyl)-4-phenylbuta-2,3-diene (11a):



11a

Yellow oil. The reaction scale is 15 mg (0.03 mmol) dibromoalkene **5d**, isolated amount is 11 mg **11a** (yield 92%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 2.34 s (3H, CH_3), 2.35 s (3H, CH_3), 7.11 d (1H$_{arom.}$, ^3J 7.9 Hz), 7.15 d (1H$_{arom.}$, ^3J 7.8 Hz), 7.21 s (1H$_{arom.}$), 7.33-7.40 m (3H$_{arom.}$), 7.54-7.56 m (2H$_{arom.}$). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 20.2 (CH_3), 21.1 (CH_3), 98.1 (C^4), 105.0 q (C^2, $J_{C\text{-}F}$ 36.0 Hz), 122.0 q (C^1, $J_{C\text{-}F}$ 276.1 Hz), 127.8, 127.9, 128.8, 129.68, 129.69, 130.4, 130.9, 132.1, 134.8, 135.8, 202.3 q (C^3, $J_{C\text{-}F}$ 3.5 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: -62.08 s (CF_3). MS (GC-MS, EI), m/z, ($I_{rel.}$, %): 366/368 $[M]^+$ (2/2), 287 (100), 272 (17), 267 (18), 247 (51), 218 (28), 202 (27), 109 (24), 95 (16), 77 (8). HRMS (MALDI-TOF): $C_{18}H_{15}F_3Br$ found 367.0314 $[M+H]^+$; calcd. 367.0304.

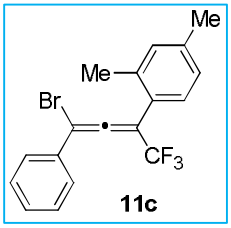
4-Bromo-1,1,1-trifluoro-2-(2,4,5-trimethylphenyl)-4-phenylbuta-2,3-diene (11b):



11b

Yellow oil. The reaction scale is 20 mg (0.04 mmol) dibromoalkene **5e**, isolated amount is 10 mg **11b** (yield 63%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 2.24 s (3H, CH_3), 2.26 s (3H, CH_3), 2.31 s (3H, CH_3), 7.04 s (1H$_{arom.}$), 7.17 s (1H$_{arom.}$), 7.33-7.40 m (3H$_{arom.}$), 7.52-7.56 m (2H$_{arom.}$). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 19.4 (CH_3), 19.6 (CH_3), 20.2 (CH_3), 97.9 (C^4), 105.0 q (C^2, $J_{C\text{-}F}$ 35.9 Hz), 122.1 q (C^1, $J_{C\text{-}F}$ 276.0 Hz), 125.3, 127.8, 128.8, 129.6, 130.1, 132.2, 132.4, 134.4, 135.1, 138.3, 202.4 q (C^3, $J_{C\text{-}F}$ 3.8 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: -62.08 s (CF_3). MS (GC-MS, EI), m/z, ($I_{rel.}$, %): 380/382 $[M]^+$ (2/2), 301 (100), 286 (18), 261 (17), 232 (18), 217 (17), 202 (11), 109 (12), 95 (8), 77 (4). HRMS (MALDI-TOF): $C_{19}H_{17}F_3Br$ found 381.0470 $[M+H]^+$; calcd. 381.0461.

4-Bromo-1,1,1-trifluoro-2-(2,4-dimethylphenyl)-4-phenylbuta-2,3-diene (11c):

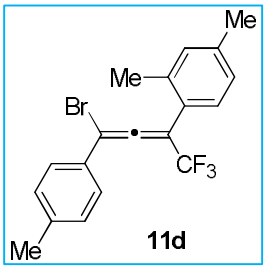


11c

Yellow oil. The reaction scale is 16 mg (0.04 mmol) dibromoalkene **5c**, isolated amount is 10 mg **11c** (yield 77%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 2.34 s (3H, CH_3), 2.35 s (3H, CH_3), 7.06-7.08 m (2H$_{arom.}$), 7.30 d (1H$_{arom.}$, ^3J 7.9 Hz), 7.34-7.40 m (3H$_{arom.}$), 7.52-7.55 m (2H$_{arom.}$). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 20.7 (CH_3), 21.3 (CH_3), 98.0 (C^4), 104.9 q (C^2, $J_{C\text{-}F}$ 36.0 Hz), 122.0 q (C^1, $J_{C\text{-}F}$ 275.9 Hz), 125.2, 126.9, 127.8, 128.8, 129.1, 129.7, 131.8, 132.2, 137.8, 139.6, 202.4 q (C^3, $J_{C\text{-}F}$ 3.6 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: -62.16 s (CF_3). MS (GC-MS, EI), m/z, ($I_{rel.}$, %): 366/368 $[M]^+$ (2/2), 287 (100), 272 (12), 247 (32), 218 (19), 202

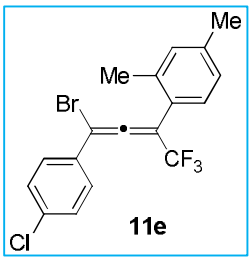
(22), 109 (19), 95 (12), 77 (6). HRMS (MALDI-TOF): $C_{18}H_{15}F_3Br$ found 367.0323 $[M+H]^+$; calcd. 367.0304.

4-Bromo-1,1,1-trifluoro-2-(2,4-dimethylphenyl)-4-(4-methylphenyl)buta-2,3-diene



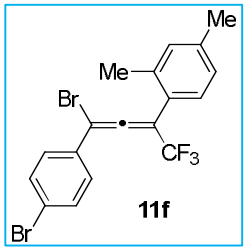
(11d): Pale yellow oil. The reaction scale is 19 mg (0.04 mmol) dibromoalkene **5h**, isolated amount is 7 mg **11d** (yield 47%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 2.33 s (3H, CH_3), 2.34 s (3H, CH_3), 2.37 s (3H, CH_3), 7.05-7.08 m ($2H_{arom.}$), 7.18 d ($2H_{arom.}$, ^3J 8.0 Hz), 7.29 d ($1H_{arom.}$, ^3J 7.8 Hz), 7.42 d ($2H_{arom.}$, ^3J 8.2 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 20.7 (CH_3), 21.3 (CH_3), 21.4 (CH_3), 98.2 (C^4), 104.7 q (C^2, $J_{C\text{-}F}$ 35.9 Hz), 122.1 q (C^1, $J_{C\text{-}F}$ 275.9 Hz), 125.4, 126.9, 127.7, 129.1, 129.3, 129.5, 131.8, 137.8, 139.5, 139.9, 202.3 q (C^3, $J_{C\text{-}F}$ 3.6 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: -62.18 s (CF_3). MS (GC-MS, EI), m/z, ($I_{rel.}$, %): 380/382 $[M]^+$ (3/3), 365/367 (14/14), 301 (100), 286 (22), 261 (42), 232 (27), 217 (25), 202 (18), 115 (17), 95 (14), 65 (8). HRMS (MALDI-TOF): $C_{19}H_{17}F_3Br$ found 381.0463 $[M+H]^+$; calcd. 381.0461.

4-Bromo-4-(4-chlorophenyl)-1,1,1-trifluoro-2-(2,4-dimethylphenyl)buta-2,3-diene



(11e): Pale yellow oil. The reaction scale is 30 mg (0.06 mmol) dibromoalkene **5j**, isolated amount is 9 mg **11e** (yield 38%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 2.34 s (6H, CH_3), 7.06-7.09 m ($2H_{arom.}$), 7.29 d ($1H_{arom.}$, ^3J 7.8 Hz), 7.35 d ($2H_{arom.}$, ^3J 8.7 Hz), 7.46 d ($2H_{arom.}$, ^3J 8.7 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 20.7 (CH_3), 21.3 (CH_3), 96.8 (C^4), 105.4 q (C^2, $J_{C\text{-}F}$ 35.9 Hz), 121.9 q (C^1, $J_{C\text{-}F}$ 276.2 Hz), 124.9, 127.0, 129.03, 129.04, 130.8, 131.9, 135.8, 137.7, 139.8, 202.4 q (C^3, $J_{C\text{-}F}$ 3.7 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: -62.16 s (CF_3). MS (GC-MS, EI), m/z, ($I_{rel.}$, %): 365/367 $[M\text{-}Cl]^+$ (29/30), 321/323 (100/35), 301 (12), 286 (40), 266 (26), 252 (21), 217 (22), 202 (21), 143 (11), 108 (33), 95 (17). HRMS (MALDI-TOF): $C_{18}H_{14}F_3BrCl$ found 400.9921 $[M+H]^+$; calcd. 400.9914.

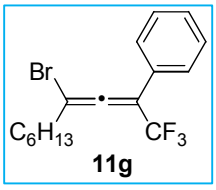
4-Bromo-4-(4-bromophenyl)-1,1,1-trifluoro-2-(2,4-dimethylphenyl)buta-2,3-diene



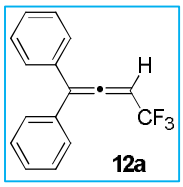
(11f): Pale yellow oil. The reaction scale is 28 mg (0.05 mmol) dibromoalkene **5l**, isolated amount is 19 mg **11f** (yield 86%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 2.34 s (6H, CH_3), 7.06-7.09 m ($2H_{arom.}$), 7.29 d ($1H_{arom.}$, ^3J 7.7 Hz), 7.40 d ($2H_{arom.}$, ^3J 8.7 Hz), 7.51 d ($2H_{arom.}$, ^3J 8.7 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 20.7 (CH_3), 21.3 (CH_3), 96.9 (C^4), 105.4 q (C^2, $J_{C\text{-}F}$ 36.1 Hz), 121.9 q (C^1, $J_{C\text{-}F}$ 275.8 Hz), 124.0, 124.8, 127.0, 129.0, 129.2, 131.3, 131.9, 132.0, 137.7, 139.8, 202.4 q (C^3, $J_{C\text{-}F}$ 3.8 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: -62.15 s (CF_3). MS (GC-MS, EI), m/z, ($I_{rel.}$, %): 365/367 $[M\text{-}HBr]^+$ (73/73), 286 (100), 271 (24),

251 (12), 217 (38), 202 (26), 126 (8), 108 (24), 95 (18). HRMS (MALDI-TOF): $C_{18}H_{14}F_3Br_2$ found 444.9397 $[M+H]^+$; calcd. 444.9409.

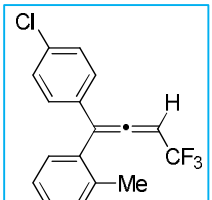
4-Bromo-1,1,1-trifluoro-2-phenyldeca-2,3-diene (11g): Pale yellow oil. The reaction scale is 12 mg (0.03 mmol) dibromoalkene **5m**, isolated amount is 6 mg **11g** (yield 60%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 0.86 t (3H, CH_3, ^3J 6.8 Hz), 1.27-1.28 m (4H, CH_2), 1.31-1.38 m (2H, CH_2), 1.55-1.62 m (2H, CH_2), 2.59 t (2H, CH_2, ^3J 7.2 Hz), 7.34-7.42 m ($3H_{arom.}$), 7.45-7.47 m ($2H_{arom.}$). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 14.1 (CH_3), 22.6 (CH_2), 27.7 (CH_2), 28.2 (CH_2), 31.5 (CH_2), 37.6 (CH_2), 100.3 (C^4), 105.4 q (C^2, $J_{C\text{-}F}$ 34.7 Hz), 122.1 q (C^1, $J_{C\text{-}F}$ 275.2 Hz), 127.7 q ($J_{C\text{-}F}$ 1.3 Hz), 128.9, 129.0, 129.2, 199.8 q (C^3, $J_{C\text{-}F}$ 4.0 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: -60.49 s (CF_3). HRMS (MALDI-TOF): $C_{16}H_{19}F_3Br$ found 347.0619 $[M+H]^+$; calcd. 347.0617.



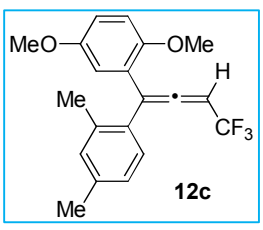
1,1,1-Trifluoro-4,4-diphenylbuta-2,3-diene (12a):[6] Colorless solid, mp 152-155°C (MeOH). The reaction scale is 18 mg (0.03 mmol) bromoalkene **8a**, isolated amount is 8 mg **12a** (yield 51%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 5.96 q (1H, C^2H, $^3J_{H\text{-}F}$ 5.7 Hz), 7.33-7.42 m ($10H_{arom.}$). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 88.7 q (C^2, $J_{C\text{-}F}$ 39.0 Hz), 117.1 (C^4), 122.7 q (C^1, $J_{C\text{-}F}$ 271.5 Hz), 128.7, 128.8, 128.9, 134.1 q ($J_{C\text{-}F}$ 1.1 Hz), 206.7 q (C^3, $J_{C\text{-}F}$ 5.9 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: -60.05 d (CF_3, $J_{H\text{-}F}$ 5.7 Hz). MS (GC-MS, EI), m/z, ($I_{rel.}$, %): 260 $[M]^+$ (82), 240 (15), 191 (100), 165 (16), 127 (10), 110 (16), 95 (27), 82 (25), 51 (9).



1,1,1-Trifluoro-4-(4-chlorophenyl)-4-(2,4-dimethylphenyl)buta-2,3-diene (12b): Pale yellow oil. The reaction scale is 23 mg (0.06 mmol) bromoalkene **8n**, isolated amount is 7 mg **12b** (yield 37%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 2.13 s (3H, CH_3), 2.37 s (3H, CH_3), 5.86 q (1H, C^2H, $^3J_{H\text{-}F}$ 5.8 Hz), 7.06-7.12 m ($3H_{arom.}$), 7.12 d ($2H_{arom.}$, ^3J 8.6 Hz), 7.29 d ($2H_{arom.}$, ^3J 8.6 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 19.9 (CH_3), 21.3 (CH_3), 88.2 q (C^2, $J_{C\text{-}F}$ 39.1Hz), 114.4 (C^4), 122.7 q (C^1, $J_{C\text{-}F}$ 271.4 Hz), 127.1, 128.6, 129.1, 130.0 q ($J_{C\text{-}F}$ 1.1 Hz), 130.1, 131.1, 132.7 q ($J_{C\text{-}F}$ 1.0 Hz), 134.4, 136.8, 138.9, 205.3 q (C^3, $J_{C\text{-}F}$ 5.8 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: -59.80 d (CF_3, $J_{H\text{-}F}$ 5.8 Hz). MS (GC-MS, EI), m/z, ($I_{rel.}$, %): 322/324 $[M]^+$ (27/9), 307/309 (16/5), 287 (100), 272 (38), 253 (41), 239 (14), 218 (63), 202 (51), 192 (13), 141 (10), 115 (12), 101 (44), 95 (27), 77 (13), 63 (11), 51 (10). HRMS (MALDI-TOF): $C_{18}H_{15}F_3Cl$ found 323.0810 $[M+H]^+$; calcd. 323.0809.



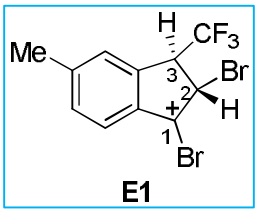
1,1,1-Trifluoro-4-(2,5-dimethoxyphenyl)-4-(2,4-dimethylphenyl)buta-2,3-diene (12c): Pale yellow oil. The reaction scale is 17 mg (0.04 mmol) bromoalkene **8u**, isolated amount is 8 mg **12b** (yield 57%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 2.17 s (3H, CH_3), 2.34 s (3H, CH_3), 3.66 s (3H, CH_3O), 3.77 s (3H,



CH_3O), 5.69 q (1H, C^2H, $^3J_{H\text{-}F}$ 6.0 Hz), 6.42 d ($1H_{arom.}$, ^4J 3.0 Hz), 6.80 dd ($1H_{arom.}$, ^3J 8.9 Hz, ^4J 3.0 Hz), 6.86 d ($1H_{arom.}$, ^3J 8.9 Hz), 7.01 d ($1H_{arom.}$, ^3J 7.7 Hz), 7.04 s ($1H_{arom.}$), 7.09 d ($1H_{arom.}$, ^3J 7.7 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 19.9 (CH_3), 21.3 (CH_3), 55.8 (OCH_3), 56.2 (OCH_3), 84.5 q (C^2, $J_{C\text{-}F}$ 38.8 Hz), 109.8 (C^4), 112.8, 113.7, 116.2, 123.3 q (C^1, $J_{C\text{-}F}$ 270.7 Hz), 124.5 q ($J_{C\text{-}F}$ 0.7 Hz), 126.9, 129.9, 131.5, 131.8 q ($J_{C\text{-}F}$ 1.3 Hz), 136.6, 138.2, 152.1, 153.7, 207.5 q (C^3, $J_{C\text{-}F}$ 6.0 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: -59.77 d (CF_3, $J_{H\text{-}F}$ 6.0 Hz). MS (GC-MS, EI), m/z, ($I_{rel.}$, %): 348 $[M]^+$ (90), 333 (100), 317 (79), 302 (20), 286 (10), 265 (9), 249 (25), 222 (19), 178 (12), 149 (10), 124 (14), 101 (10), 89 (11), 77 (9), 55 (7). HRMS (MALDI-TOF): $C_{20}H_{20}F_3O_2$ found 349.1413 $[M+H]^+$; calcd. 349.1410.

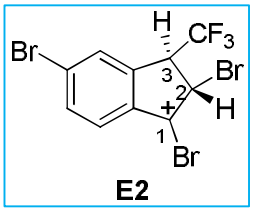
NMR Data of Cations E1-E3, G1-G3 in TfOH.

Cation *trans*-**E1** was generated from alcohol **1b** or dibromoindene **3b** in TfOH at -20°C for 15 min. **^{1}H NMR** (400 MHz, TfOH) δ, ppm: 2.85 s (3H, CH_3), 4.72 q (1H, C^3H, $^3J_{H\text{-}F}$ 7.8 Hz), 6.00 s (1H, C^2H), 8.02-8.05 m ($2H_{arom.}$), 8.52 d ($1H_{arom.}$, ^3J 8.7 Hz). **^{13}C NMR** (100 MHz, TfOH) δ, ppm: 28.0 (CH_3), 50.4 q (C^2, $J_{C\text{-}F}$ 1.7 Hz), 60.6 q (C^3, $J_{C\text{-}F}$ 30.3 Hz), 124.5 q (CF_3, $J_{C\text{-}F}$ 278.3 Hz), 132.2, 140.0, 140.5, 146.7, 163.8, 185.1, 215.0 (C^+). **^{19}F NMR** (376 MHz, TfOH) δ, ppm: -69.60 d (CF_3, $J_{H\text{-}F}$ 7.8 Hz).



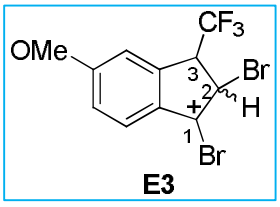
E1

Cation *trans*-**E2** was generated from alcohol **1d** or dibromoindene **3d** in TfOH at 20°C for 15 min. **^{1}H NMR** (400 MHz, TfOH) δ, ppm: 4.74 q (1H, C^3H, $^3J_{H\text{-}F}$ 7.8 Hz), 5.59 d (1H, C^2H, $^3J_{H\text{-}F}$ 1.3 Hz), 8.21 d ($1H_{arom.}$, ^3J 8.6 Hz), 8.28 s ($1H_{arom.}$), 8.31 d ($1H_{arom.}$, ^3J 8.6 Hz). **^{13}C NMR** (100 MHz, TfOH) δ, ppm: 39.0 q (C^2, $J_{C\text{-}F}$ 2.7 Hz), 57.6 q (C^3, $J_{C\text{-}F}$ 31.6 Hz), 125.1 q (CF_3, $J_{C\text{-}F}$ 280.7 Hz), 129.1, 133.5, 134.3, 139.6, 152.2, 158.0, 213.8 (C^+). **^{19}F NMR** (376 MHz, TfOH) δ, ppm: -70.25 d (CF_3, $J_{H\text{-}F}$ 7.8 Hz).



E2

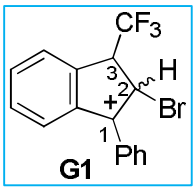
Cations *cis*-**E3** and *trans*-**E3** was generated from alcohol **1e** or dibromoindene **3e** in TfOH at 20°C for 15 min. *Cis*-**E3**: **^{1}H NMR** (400 MHz, TfOH, measured in a mixture with *trans*-**E3**) δ, ppm: 4.51 s (3H, CH_3), 4.78 qd (1H, C^3H, $^3J_{H\text{-}F}$ 8.3 Hz, ^3J 5.3 Hz), 5.88 d (1H, C^2H, ^3J 5.3 Hz), 7.52 s ($1H_{arom.}$), 7.56 d ($1H_{arom.}$, ^3J 9.7 Hz), 8.37-8.39 m ($1H_{arom.}$). **^{13}C NMR** (100 MHz, TfOH, measured in a mixture with *trans*-**E3**) δ, ppm: 50.1 (C^2), 53.8 q (C^3, $J_{C\text{-}F}$ 31.6 Hz), 62.8, 116.8, 124.3 q (CF_3, $J_{C\text{-}F}$ 278.9 Hz), 127.9, 141.0, 142.2, 164.4 q ($J_{C\text{-}F}$ 1.5 Hz), 188.1, 189.8 (C^+). **^{19}F NMR** (376 MHz, TfOH, measured in a mixture with *trans*-**E3**) δ, ppm: -63.76 d (CF_3, $J_{H\text{-}F}$ 8.3 Hz). *Trans*-**E3**: **^{1}H NMR** (400 MHz, TfOH, measured in a mixture with *cis*-**E3**) δ, ppm: 4.53 s (3H, CH_3), 4.68 q (1H, C^3H, $^3J_{H\text{-}F}$ 8.2 Hz), 5.81 s (1H, C^2H), 7.52 s ($1H_{arom.}$), 7.59 dd ($1H_{arom.}$, ^3J



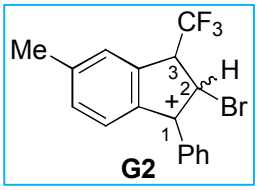
E3

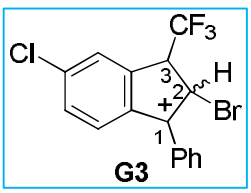
9.5 Hz, ^4J 1.5 Hz), 8.38 d (1H$_{arom.}$, ^3J 9.5 Hz). **^{13}C NMR** (100 MHz, TfOH, measured in a mixture with *cis*-**E3**) δ, ppm: 49.9 q (C^2, $J_{C\text{-}F}$ 2.3 Hz), 60.0 q (C^3, $J_{C\text{-}F}$ 31.1 Hz), 63.0, 116.9 q ($J_{C\text{-}F}$ 1.4 Hz), 124.7 q (CF$_3$, $J_{C\text{-}F}$ 278.7 Hz), 128.3, 142.0, 142.1, 164.5 q ($J_{C\text{-}F}$ 2.0 Hz), 188.6, 190.0 (C$^+$). **^{19}F NMR** (376 MHz, TfOH, measured in a mixture with *cis*-**E3**) δ, ppm: -69.93 d (CF$_3$, $J_{H\text{-}F}$ 8.2 Hz).

Cations *cis*-**G1** and *trans*-**G1** was generated from bromoindene **6a** in TfOH at 20°C for 15 min. *Cis*-**G1**: **^{1}H NMR** (400 MHz, TfOH, measured in a mixture with *trans*-**G1**) δ, ppm: 4.88-4.94 m (1H, C^{3}H), 6.46 d (1H, C^{2}H, ^3J 4.4 Hz), 7.96-8.02 m (3H$_{arom.}$), 8.13-8.19 m (2H$_{arom.}$), 8.37-8.41 m (1H$_{arom.}$), 8.69 d (2H$_{arom.}$, ^3J 7.7 Hz), 8.83 d (1H$_{arom.}$, ^3J 7.9 Hz). **^{19}F NMR** (376 MHz, TfOH, measured in a mixture with *trans*-**G1**) δ, ppm: -65.54 d (CF$_3$, $J_{H\text{-}F}$ 8.0 Hz). *Trans*-**G1**: **^{1}H NMR** (400 MHz, TfOH, measured in a mixture with *cis*-**G1**) δ, ppm: 4.93 q (1H, C^{3}H, $^3J_{H\text{-}F}$ 7.8 Hz), 6.39 s (1H, C^{2}H), 7.98-8.02 m (2H$_{arom.}$), 8.13-8.19 m (2H$_{arom.}$), 8.37-8.41 m (1H$_{arom.}$), 8.60-8.64 m (3H$_{arom.}$), 8.79 d (1H$_{arom.}$, ^3J 8.2 Hz). **^{13}C NMR** (100 MHz, TfOH) δ, ppm: 44.3 q (C^2, $J_{C\text{-}F}$ 2.9 Hz), 61.4 q (C^3, $J_{C\text{-}F}$ 30.6 Hz), 125.2 q (CF$_3$, $J_{C\text{-}F}$ 291.6 Hz), 131.9, 133.7, 135.7, 136.2, 140.2, 141.7, 142.2, 149.8, 152.7, 160.1 q ($J_{C\text{-}F}$ 1.6 Hz), 213.9 (C$^+$). **^{19}F NMR** (376 MHz, TfOH, measured in a mixture with *cis*-**G1**) δ, ppm: -71.13 d (CF$_3$, $J_{H\text{-}F}$ 7.8 Hz).



Cations *cis*-**G2** and *trans*-**G2** was generated from bromoindene **6d** in TfOH at 20°C for 15 min. *Cis*-**G2**: **^{1}H NMR** (400 MHz, TfOH, measured in a mixture with *trans*-**G2**) δ, ppm: 2.86 s (3H, CH$_3$), 4.82-4.88 m (1H, C^{3}H), 6.36 d (1H, C^{2}H, ^3J 3.7 Hz), 7.96-8.07 m (5H$_{arom.}$), 8.19-8.22 m (1H$_{arom.}$), 8.41-8.65 m (2H$_{arom.}$). **^{13}C NMR** (100 MHz, TfOH, measured in a mixture with *trans*-**G2**) δ, ppm: 25.0 (CH$_3$), 43.4 (C^2), 61.4 q (C^3, $J_{C\text{-}F}$ 27.3 Hz), 125.2 q (CF$_3$, $J_{C\text{-}F}$ 280.1 Hz), 131.5 q ($J_{C\text{-}F}$ 1.9 Hz), 132.6, 132.8, 133.3, 136.1, 138.9, 140.8, 140.9, 145.4, 170.2, 218.1 (C$^+$). **^{19}F NMR** (376 MHz, TfOH, measured in a mixture with *trans*-**G2**) δ, ppm: -64.29 d (CF$_3$, $J_{H\text{-}F}$ 7.4 Hz). *Trans*-**G2**: **^{1}H NMR** (400 MHz, TfOH, measured in a mixture with *cis*-**G2**) δ, ppm: 2.88 s (3H, CH$_3$), 4.83 q (1H, C^{3}H, $^3J_{H\text{-}F}$ 8.0 Hz), 6.31 s (1H, C^{2}H), 7.96-8.07 m (3H$_{arom.}$), 8.19-8.22 m (1H$_{arom.}$), 8.41-8.65 m (4H$_{arom.}$). **^{13}C NMR** (100 MHz, TfOH, measured in a mixture with *cis*-**G2**) δ, ppm: 25.7 (CH$_3$), 44.5 q (C^2, $J_{C\text{-}F}$ 1.6 Hz), 60.9 q (C^3, $J_{C\text{-}F}$ 30.5 Hz), 125.3 q (CF$_3$, $J_{C\text{-}F}$ 280.3 Hz), 131.8 q ($J_{C\text{-}F}$ 1.3 Hz), 133.0, 135.0, 138.2, 138.6, 140.0, 141.2, 146.8, 160.9, 173.2, 209.3 (C$^+$). **^{19}F NMR** (376 MHz, TfOH, measured in a mixture with *cis*-**G2**) δ, ppm: -70.19 d (CF$_3$, $J_{H\text{-}F}$ 7.8 Hz).





Cations *cis*-**G3** and *trans*-**G3** was generated from bromoindene **6h** in TfOH at 20°C for 15 min. *Cis*-**G3**: **^{1}H NMR** (400 MHz, TfOH, measured in a mixture with *trans*-**G3**) δ, ppm: 4.87-4.92 m (1H, C^{3}H), 6.40 d (1H,

C^2H, ^3J 4.5 Hz), 7.94-7.80 m ($2H_{arom.}$), 8.06 dd ($1H_{arom.}$, ^3J 8.8 Hz, ^4J 1.2 Hz), 8.10-8.13 m ($1H_{arom.}$), 8.35-8.38 m ($1H_{arom.}$), 8.63 d ($2H_{arom.}$, ^3J 7.8 Hz), 8.71 d ($1H_{arom.}$, ^3J 8.8 Hz). **^{19}F NMR** (376 MHz, TfOH, measured in a mixture with *trans*-**G3**) δ, ppm: -65.24 d (CF_3, J_{H-F} 8.0 Hz). *Trans*-**G3**: **^{1}H NMR** (400 MHz, TfOH, measured in a mixture with *cis*-**G3**) δ, ppm: 4.88 q (1H, C^3H, $^3J_{H-F}$ 7.9 Hz), 6.34 s (1H, C^2H), 7.97 d ($2H_{arom.}$, ^3J 7.8 Hz), 8.12 dd ($1H_{arom.}$, ^3J 8.8 Hz, ^4J 1.7 Hz), 8.16 s ($1H_{arom.}$), 8.35-8.38 m ($1H_{arom.}$), 8.57 d ($2H_{arom.}$, ^3J 7.8 Hz), 8.70 d ($1H_{arom.}$, ^3J 8.8 Hz). **^{13}C NMR** (100 MHz, TfOH) δ, ppm: 44.3 q (C^2, J_{C-F} 2.4 Hz), 60.9 q (C^3, J_{C-F} 30.9 Hz), 125.1 q (CF_3, J_{C-F} 296.9 Hz), 132.5, 133.7, 135.4, 137.4, 138.5, 141.4, 141.6, 149.4, 155.4, 164.0, 210.3 (C^+). **^{19}F NMR** (376 MHz, TfOH, measured in a mixture with *cis*-**G3**) δ, ppm: -70.97 d (CF_3, J_{H-F} 7.9 Hz).

References

1. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Cryst*. **2009**, *42*, 339-341.

2. *SHELXS*; Sheldrick, G. M. *Acta Cryst.* **2008**, *A64*, 112-122.

3. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *GAUSSIAN 03, Revision D.02*; Gaussian, Inc., Wallingford CT, **2004**.

4. Okano, T.; Matsubara, H.; Kusukawa, T.; Fujuta, M. *J. Organomet. Chem.* **2003**, *676*, 43-48.

5. Shen Y.; Zhang Y. *Org. Lett.,* **2001**, *3* (18), 2805-2806.

6. Ji, Y.-L.; Luo, J.-J.; Lin, J.-H.; Xiao, J.-C.; Gu; Y.-C. *Org. Lett*. **2016**, *18*, 1000−1003.