Organic & Biomolecular Chemistry

RSC Publishing

PAPER

View Article Online
View Journal | View Issue

Cite this: *Org. Biomol. Chem.*, 2013, **11**, 8103

Preparations of SF_5- and CF_3-substituted arenes utilizing the 7-oxabicyclo[2.2.1]hept-2-ene synthones†

Maxim V. Ponomarenko,*[a] Katrin Lummer,[a] Andrey A. Fokin,[b] Yurii A. Serguchev,[c] Bassem S. Bassil[a] and Gerd-Volker Röschenthaler[a]

Received 30th July 2013,
Accepted 10th October 2013

DOI: 10.1039/c3ob41560k

www.rsc.org/obc

The synthesis of SF_5- and CF_3-substituted benzenes and naphthalenes from various 7-oxanorbornene derivatives utilizing SF_5Cl and CF_3I radical addition reactions, followed by dehydrohalogenation and aromatization, is reported. The differences in the behavior of the SF_5- and CF_3-containing intermediates under basic and acidic conditions are discussed. The experimentally observed high regioselectivities of the formation of 2-R_F-substituted-1-naphthols agree well with the *ab initio* computations, revealing the first example of the $SF_5\cdots HO$ hydrogen bonding.

Introduction

Recent discoveries of CF_3-substituted aromatics among biologically active compounds have stimulated the development of new approaches towards the synthesis of trifluoromethylated arenes.[1] The advantages of the arenes containing pentafluoro-λ^6-sulfanyl substituent (SF_5),[2] which was recently labeled a "super CF_3 function",[2d,g] attract substantial interest with respect to their potential as materials,[2d,g,3] pharmaceuticals,[2a,4] and agrochemicals.[2b] However, the number of SF_5-containing compounds is limited by poor availability of the SF_5 sources or building blocks.

Several approaches towards the preparation of pentafluoro-λ^6-sulfanyl benzenes have been developed. The most common are based on the fluorination of diaryl disulfides or aryl thiols with AgF_2 or XeF_2,[5] F_2,[6] or with excess of chlorine and potassium fluoride resulting in the formation of [chloro(tetrafluoro)-λ^6-sulfanyl]aryles. The latter were converted to the SF_5-containing products in good yields utilizing zinc fluoride, HF-pyridine complex, excess of anhydrous hydrofluoric acid, or SbF_5.[7] The functionalizations of the obtained SF_5-aromatics were intensively explored recently.[6b,8] The alternative synthetic approach is based on the radical additions of SF_5X (X = Br, Cl) to multiple bonds (cyclohexenes, acetylene, and sulfolene), followed by the conversion of the corresponding adducts.[9]

The ring-opening reactions of the 7-oxabicyclo[2.2.1]hept-2-ene (7-oxanorbornene) derivatives involving the cleavage of the oxygen bridge[10] are useful for the preparations of functionalized cyclohexene derivatives,[11] and arenes,[12] as well as various natural products and their analogues.[13] However, to the best of our knowledge, the additions[14] to 7-oxanorbornene have never been applied for the preparation of perfluoro-arene derivatives. The only example includes the preparation of 3-pentafluoro-λ^6-sulfanyl furanes from the adducts of SF_5Cl with 5-cyano-7-oxanorbornenes.[15]

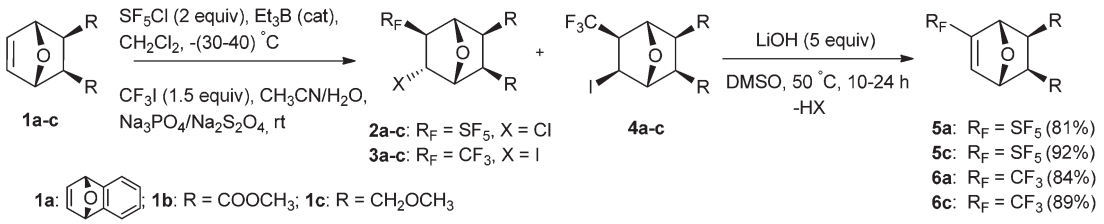
Alternatively, 2-pentafluoro-λ^6-sulfanyl naphthalene was obtained in three steps through the addition of SF_5Cl to benzobarralene followed by dehydrochlorination and elimination of the ethylene bridge *via* a sequence of cycloadditions and retrocycloadditions.[16]

Results and discussion

Herein we present the synthesis of SF_5- and CF_3-benzenes and naphthalenes from the readily available[11e,17] 7-oxanorbornene derivatives **1a–c** utilizing the radical additions of SF_5Cl[18] and CF_3I,[19] respectively. The selective *exo*-addition of the electrophilic radicals $SF_5^{\bullet}$ and $CF_3^{\bullet}$ to the double bond and the predominant *endo*-abstractions of the halogens (Cl, I) lead to the respective adducts **2a–c** and **3a–c** in good preparative yields (Scheme 1). Minute amounts of *exo*/*exo*-addition products (**4a–c**) were observed in the reaction of CF_3I with **1a–c** (Scheme 1, Table 1, entries 4–6). The *exo*–*endo* stereospecificity of the addition of SF_5Cl is due to the steric demand of the SF_5-group.[20] The stereochemistry of **2**, **3** and **4c** was proven by 1- and 2D NMR spectroscopy (see the ESI† for details). The

[a]*School of Engineering and Science, Jacobs University Bremen gGmbH, Campus Ring 1, 28759 Bremen, Germany. E-mail: m.ponomarenko@jacobs-university.de; Fax: +49 421 2003229; Tel: +49 421 2003651*
[b]*Department of Organic Chemistry, Kiev Polytechnic Institute, pr. Pobedy 37, 03056 Kiev, Ukraine*
[c]*Institute of Organic Chemistry, NAS of Ukraine, 5 Murmanskaya Str., 02094 Kiev, Ukraine*

†Electronic supplementary information (ESI) available: Copies of ^1H, ^{13}C, ^{19}F NMR, and 2D spectra of synthesized products, X-ray structures of **8**, **10a**, **14c**. CCDC 951078–951080. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3ob41560k



Scheme 1 The radical additions to 7-oxanorbornenes **1a–c** with further dehydrohalogenations.

Table 1 The radical additions of SF_5Cl and CF_3I to 7-oxanorbornenes **1a–c**

#	Starting olefin	Reagent	Time (h)	Isolated yield (%) **2, 3** (*exo–endo*)	**4a–c** (*exo–exo*)
1	**1a**	SF_5Cl	10	84	—
2	**1b**	SF_5Cl	18	79	—
3	**1c**	SF_5Cl	10	96	—
4	**1a**	CF_3I	40	90	~1[a]
5	**1b**	CF_3I	48	81	5[a]
6	**1c**	CF_3I	40	70 (84)[a]	5 (14)[a]

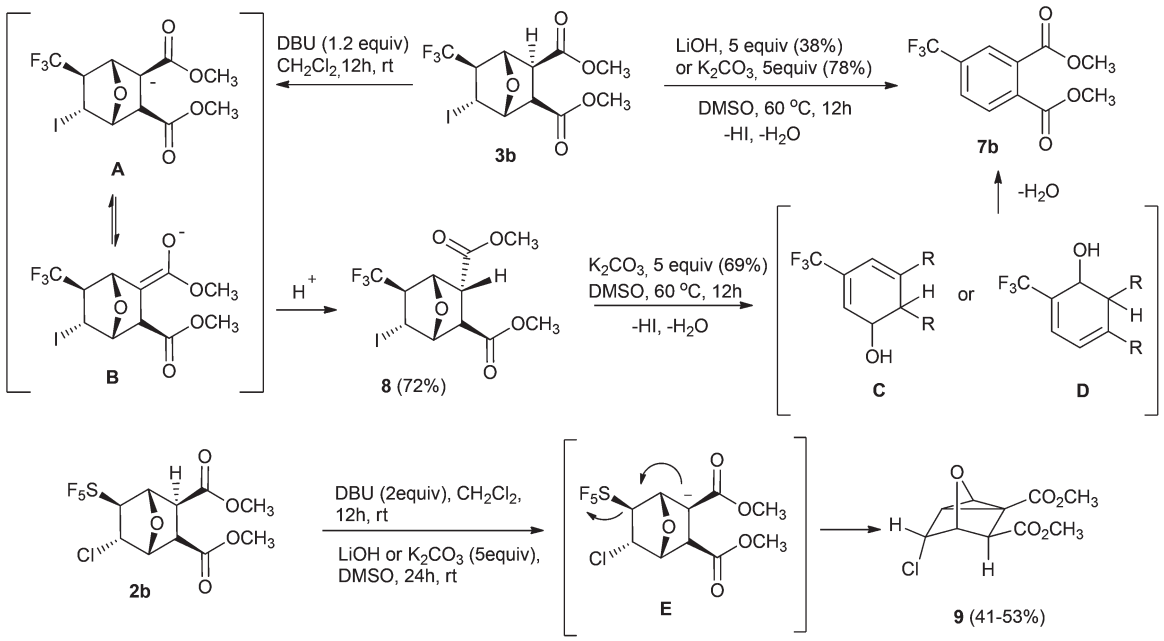
[a] Determined by ^{19}F NMR.

reaction of SF_5Cl with the Diels–Alder adduct of furan and maleic anhydride (not shown) gave only a 56% yield of the desired radical addition product, which was converted to **2b** (90% yield) by refluxing in methanol with catalytic amounts of sulfuric acid.

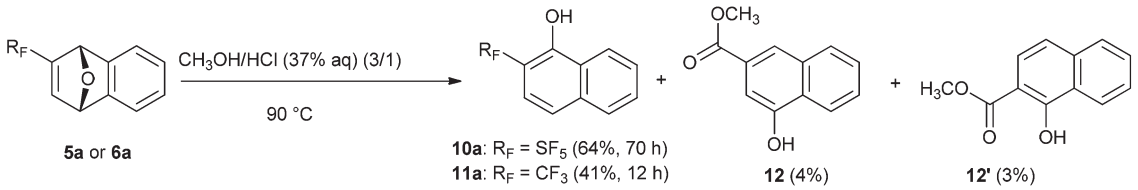
Dehydrohalogenations of **2a**, **c** and **3a**, **c** with LiOH (5 eq.) in DMSO occurred with high selectivity, providing olefins **5a**, **c** and **6a**, **c**, respectively (Scheme 1). The mixture of the stereoisomers **3c** and **4c** can be used for the elimination step; however, the reaction rates vary slightly for each stereoisomer. We have found that the *anti*-elimination of HI from **4c** is *ca.* 2 times faster than that for the *syn*-elimination from **3c** (see the ESI† for details).

The behavior of adducts **2b** and **3b** under the basic conditions is determined by the presence of the *endo*-protons at the α-position to the carboxylic groups. The treatment of **3b** with LiOH or K_2CO_3 in DMSO results in the aromatization to **7b** (Scheme 2). When the reaction was monitored by ^1H NMR spectroscopy, the formation of an intermediate **8** was detected. Under the ambient reaction conditions with DBU, the isomer **8** was isolated in 72% yield. The structure of **8** was confirmed by X-ray crystal structure analysis (see the ESI†). We conclude that the aromatization of **3b** occurs *via* an initially formed carbanionic intermediate **A**, which undergoes the rearrangement through a resonance-stabilized enolate **B**, to give the more thermodynamically stable *exo*,*endo*-dimethylcarboxylate **8** as an intermediate.

According to the literature data,[21] the subsequent base-induced *endo*- and *exo*-α-deprotonations of 7-oxabicyclo[2.2.1]-heptane-2 carboxylates are viable. As a result of the latter, and HI elimination, the further aromatization of **8** to **7b** may proceed through either intermediate **C** or **D**. Thus, the



Scheme 2 Base-catalyzed transformations of **2b** and **3b**.



Scheme 3 The preparation of R_F-naphthols **10–11a** by the acid-catalyzed ring-opening.

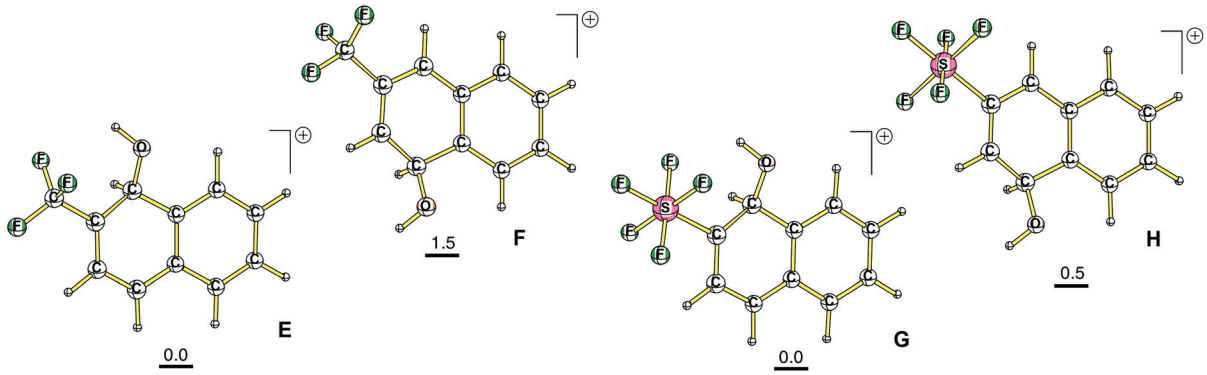


Fig. 1 The MP2/cc-pVDZ (kcal mol^{-1}) relative energies of the cations formed after the proton-induced ring-openings of **5a** and **6a**.

treatment of **8** with K_2CO_3 in DMSO leads to the aromatic product **7b** in good yield (Scheme 2).

The presence of SF_5-group in adduct **2b** changed the reaction course dramatically as we isolated only a nortricyclic compound **9** after the treatment with DBU in CH_2Cl_2, and LiOH or K_2CO_3 in DMSO (Scheme 2). The formation of **9** is likely to occur *via* the α-*endo*-deprotonation to anion **E**, which undergoes cyclization accompanied by the γ-elimination of the SF_5-anion, which is the better leaving group than the CF_3-anion.[22]

In order to isomerize **5a** and **6a** into the corresponding aromatic products, we tested several acid-promoted ring-opening reactions. The isomerization of the SF_5-containing 7-oxanorbornene derivative **5a** proceeds slowly, giving only one regioisomer of the SF_5-substituted 2-pentafluoro-λ^6-sulfanyl-1-naphthol (**10a**) in 64% yield after heating at 90 °C in methanol–HCl (Scheme 3). The ring-opening of **6a** under similar conditions resulted in the formation of CF_3-naphthol **11a**, together with the traces of **12** and **12′**, which resulted from the acidic hydrolysis[6b,23] of the CF_3-group.

The regiospecificities of the formation of 2-R_F-substituted-1-naphthols **10a** and **11a** in the acid-catalyzed ring-opening reactions of **5a** and **6a** are not obvious[12d-f] and cannot be explained by the participation of both rings in charge delocalization, but rather by electron-withdrawing properties of the perfluorinated substituents SF_5 and CF_3. We computed[24] the relative stabilities of the respective intermediates and found that cations **E** and **G** are more stable than their counterparts **F** and **H** (Fig. 1). We conclude that the regioselectivities of the ring-opening of **5a** and **6a** are determined by the electron-withdrawing effect of the fluorine-containing substituents that destabilize the cationic intermediates of type **F** and **H**. Importantly, the cations **E** and **G** are *additionally stabilized by the intramolecular F···HO hydrogen bonding*.

It is known that the CF···HO hydrogen bonding can influence the properties of fluorine containing organic compounds.[25] However, due to the poor polarizability of the C–F bond in organic fluorides the weak hydrogen bonding[26] enhances only selected molecular structures and conformations.[25b,27] To the best of our knowledge, there is no indication for intramolecular F···HO interactions in the organic compounds bearing the SF_5-group. It has been shown that rotation around the SF_5C–COH bond of saturated alcohols is controlled by the SF_5-substituent,[28] but this influence was attributed to the stereoelectronic effects, rather than to the SF···HO bonding, which was estimated as only 0.08 kcal mol^{-1}.[28b]

To our surprise, in the ^{1}H NMR spectra of **10a** and **11a** in $CDCl_3$ we observed the distinct multiplets of the OH protons due to spin–spin coupling with SF_5- and CF_3-substituents, correspondingly. The signal of the OH proton of **10a** is observed as a quintet ($^5J_{HF}$ = 4.9 Hz, 6.77 ppm) resulting from the coupling on four equatorial fluorine atoms (F_{eq}) of the SF_5-group. The exceptionally sharp quartet at 6.32 ppm with $^5J_{HF}$ = 5.1 Hz was observed for the hydroxyl proton of **11a**. This is in contrast to the *ortho*-CF_3-substituted phenols and 2-naphthols that typically display the OH-proton singlets in their ^{1}H NMR spectra.[29] The observed constants are too large for through bond coupling and may be attributed to the through-space intramolecular interaction only. The multiplets of the OH-protons of **10a** and **11a** disappeared in DMSO-d_6 due to the formation of the strong OH···DMSO hydrogen bond where the sharp singlets at 10–11 ppm were observed instead.

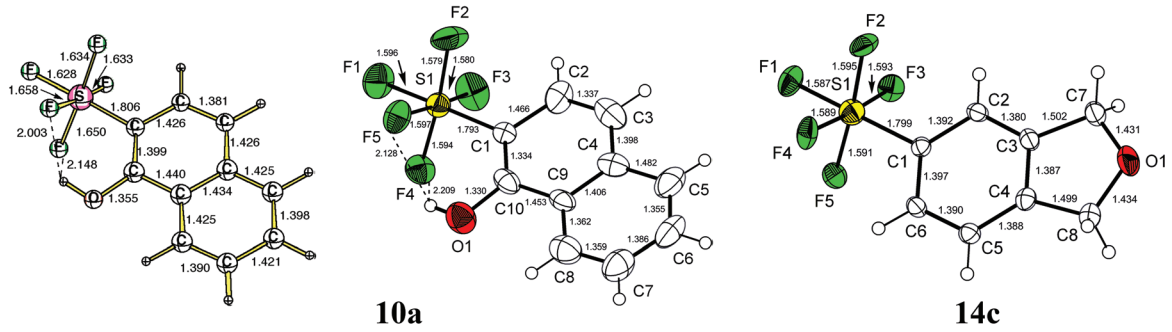


Fig. 2 The MP2/cc-pVDZ optimized geometry of **10a** (left, bond distances in Å) and experimental X-ray crystal structures of **10a** and **14c**.

In order to detect the SF···HO interactions in the solid state, we carried out an X-ray crystallographic study of **10a**. A block-like single crystal of **10a** appropriate for the X-ray analysis was grown from an *n*-hexane–CH_2Cl_2 solution. The crystal structure of **10a** (Fig. 2) shows a typical SF_5-group geometry, which is similar to that previously reported for SF_5-substituted aromatics,[6b,30] as well as to the X-ray structure of the product **14c** (Fig. 2). The S–F bond lengths of **10a** are approximately 1.58–1.60 Å, and 1.793(9) Å distance is observed for the C–S bond. The equatorial fluorine atoms are directed slightly away from the naphthalene ring resulting in the value of 86.5–87.8° for the F–S–F angles between the equatorial and axial fluorine atoms of the SF_5-group. The equatorial fluorine atoms are staggered to the relative naphthalene plane forming the F_{eq}–S–C–C dihedral angles of 47–48°. Accordingly, the hydrogen atom of the hydroxyl group is directed towards the SF_5-group, and adjacent to the two equatorial fluorine atoms within distances of 2.209 Å (OH···F_{eq}^4) and 2.128 Å (OH···F_{eq}^5) forming the F_{eq}···H–O angles of about 129.5°. Both of these OH···F_{eq} distances are much shorter than the sum of the van der Waals radii of hydrogen and fluorine atoms (2.67 Å).[31]

The O···F_{eq} distances (O···F_{eq}^4 = 2.802 Å; O···F_{eq}^5 = 2.727 Å) in **10a** are also shorter than the sum of the van der Waals radii of oxygen (1.52 Å) and fluorine atoms (1.47 Å).[31] These distances are conclusive evidence of the SF···HO hydrogen bonding in **10a** and are in perfect agreement with the MP2/cc-pVDZ optimized geometry of **10a** (Fig. 2). We have found that the C–O rotamer of **10a** with an opposite location of the OH fragment is *ca.* 5.5 kcal mol^{-1} less stable.

The compound **10a** crystallizes in $P\bar{1}$ space group with four molecules occupying the unit cell (see the ESI†). In the solid state the molecules of **10a** make couples, in which the molecules are oriented to each other by the intermolecular interaction of the SF_5-group and the OH-group lying in almost parallel planes of the naphthol moieties. The distance between the nearest F_{eq} atom of the SF_5-group of one molecule and the OH hydrogen of the other (2.56 Å) is close to the van der Waals radii of hydrogen and fluorine atoms.

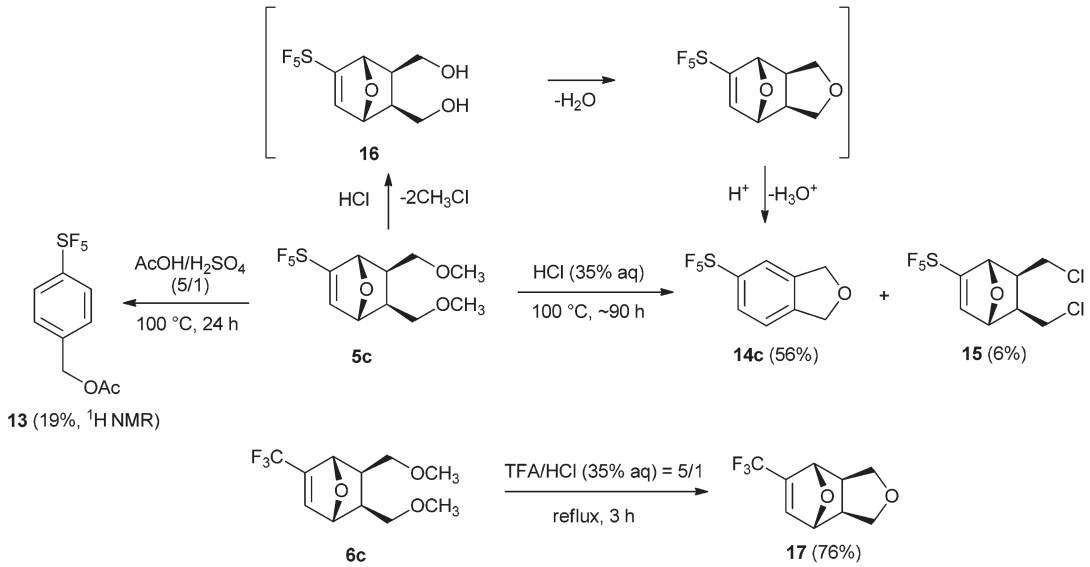
As additional evidence of the S–F_{eq}···HO hydrogen bonding in the solid state of **10a**, the ν_{OH} was observed as a sharp band at 3633 cm^{-1} in the IR spectrum measured in KBr unlike the broadening and red-shifting band of 1-naphthol caused by intermolecular hydrogen bond in the crystal.

Unlike **5a** and **6a**, compound **5c** undergoes the acid-induced ring-opening, followed by aromatization only under harsh conditions that give a number of side products. Treatment of **5c** with a mixture of acetic and sulfuric acids (5/1) at 100 °C for 24 h is accompanied by tarring and only one SF_5-containing aromatic product **13** was identified (Scheme 4). In the reaction of **5c** with hydrochloric acid (35% aq.) at 100 °C the starting compound was completely consumed in *ca.* 90 h, giving the main product **14c**, which was isolated from the complex reaction mixture in 56% yield (Scheme 4). The formation of **14c** likely occurs through a preliminary hydrolysis of the CH_3O-groups to the corresponding dialcohol **16** with further cleavage of the C–O bond of the bicycle followed by the dehydration. The hydrochlorination of the intermediate **16** yielded the product **15** (Scheme 4). Alternatively, the monochlorination of **5c** and further intramolecular S_N2 substitution also can give **14c**. However, this is less probable under acidic conditions.

All our attempts to aromatize the CF_3-substituted compound **6c** failed. For instance, the exposure of **6c** with hydrochloric or Lewis acids, such as BF_3-etherate or $TiCl_4$/Zn-system in THF, at 80–100 °C led to full decomposition of the starting material. The corresponding reaction mixtures were only contaminated by CF_3-containing, and unidentified aromatic products. In the reaction with BF_3-etherate only ethyl benzoate as an aromatic product was isolated in 4% yield. Refluxing in the mixture of trifluoroacetic and hydrochloric acids resulted in the formation of a tricyclic product **17** in high yield (Scheme 4), clearly indicating that hydrolysis of the CH_3O-group followed by the formation of the new cyclic ether proceeds faster than the cleavage of C–O bond of the 7-oxanorbornene cage. The addition of hydrochloric or sulfuric acids into the trifluoroacetic acid solution of **17** and long exposure under elevated temperature led to complicated reaction mixtures.

Conclusions

We have found that the radical additions of SF_5Cl and CF_3I to the double bond of 7-oxanorbornene is a useful tool for the



Scheme 4 The acid-catalyzed transformations of **5c** and **6c**.

introduction of SF_5- and CF_3-substituents. The products obtained from further transformations of the adducts depend on the functional groups present in the structures. The reactions of **2a**, **c** and **3a**, **c** with LiOH led to the formation of dehydrohalogenation products **5a**, **c** and **6a**, **c** in good yields. Subsequent treatment of **5a**, **c** and **6a** with Brønsted acids gives the products of aromatization **10a**, **14c**, and **11a**, respectively. The behavior of the adducts of SF_5Cl and CF_3I and dimethyl 7-oxanorbornene-2,3-dicarboxylate (**1b**) under basic conditions is determined by the *endo*-protons at the α-position to the carboxylic groups. We found dramatic differences in the reactions of SF_5-product **2b** and CF_3-containing product **3b** with bases. Reactions of **3b** with LiOH or K_2CO_3 occur *via* the intermediate formation of the rearrangement product **8**, which undergoes the aromatization to **7b**. The treatment of **2b** with bases (DBU, LiOH, and K_2CO_3) leads to the γ-elimination of the SF_5-group giving the nortricyclic product **9**.

Computations show that the high regioselectivities of the formation of 2-R_F-substituted-1-naphthols **10a** and **11a** in the aromatization reactions are determined by the stability of the intermediate carbocations formed after cleavage of the C–O bond of the 7-oxanorbornane moiety. The products are additionally stabilized by the intramolecular Ar–R_F···HO hydrogen bonding, which is shown for the first time for the SF_5···HO moiety by the example of **10a**.

Experimental section

Compounds **1a–c** were prepared according to literature procedures.[11e,17] All reagents from commercial suppliers were used without further purification. ^1H (399.78 or 200.13 MHz), ^{13}C (100.53 or 50.32 MHz), and ^{19}F (376.17 or 188.31) NMR spectra were recorded on a Jeol ECX-400 and Bruker DPX-200 using TMS or CCl_3F as an internal standard. Column chromatography was performed on Kieselgel Merck 60 (230–400 mesh).

Single crystals were each mounted on a Hampton cryo-loop for indexing and intensity data collection at 173 K (compound **10a**, CCDC 951079) and 100 K (compounds **8**, CCDC 951078, and **14c**, CCDC 951080) using Mo Kα radiation (λ = 71.073 pm). Lorentz and polarization corrections were applied, and an absorption correction was performed using the SADABS program.[32] Direct methods were used for structure solution of all structures (SHELXS-97). Structural refinement was obtained from successive Fourier maps (SHELXL-97).[33] All heavy atoms (C, O, F, I, and S) were refined anisotropically, and the hydrogen atoms were either found through calculated constrained positions or directly. In order to prove the hydrogen bonding in **10a** the OH-hydrogen atom was found directly and refined isotropically.

General procedure for SF_5Cl addition to 1a–c

In a 3-necked flask equipped with a dry ice condenser and an argon inlet **1a** (1.0 g, 6.94 mmol) was dissolved in dry dichloromethane and cooled down to −40 °C. Then SF_5Cl (2.25 g, 13.9 mmol, 2 equiv.) was condensed into the solution and while stirring at −40 °C, Et_3B (0.1 equiv., 1 M in hexane) was added. The solution was stirred for 10–18 h and then warmed to rt. The solvent was evaporated, the crude product was diluted with 50 mL of CH_2Cl_2, washed with water (2 × 5 mL), and dried under sodium sulfate. After evaporation of the solvent the pure product **2a** (1.79 g, 84%) was isolated by filtration through SiO_2 (CH_2Cl_2).

***endo*-2-Chloro-*exo*-3-(pentafluoro-λ^6-sulfanyl)-1,2,3,4-tetrahydro-1,4-epoxynaphthalene (2a).** Yellow oil; ^1H NMR (400 MHz, $CDCl_3$): δ 7.47–7.43 (m, 1H), 7.41–7.37 (m, 1H), 7.35–7.30 (m, 2H), 5.89 (s, 1H, H^4), 5.46 (d, $^3J_{1,2}$ = 4.9 Hz, 1H, H^1), 5.01 (t, $^3J_{2,1,3}$ = 4.9 Hz, 1H, H^2), 3.86 (quin-d, $^3J_{3,F}$ = 6.4 Hz,

$^3J_{3,2}$ = 4.5 Hz, 1H, H^3); ^{13}C NMR (101 MHz, $CDCl_3$): δ 141.7 (quin, ^4J = 1.2 Hz, Ar), 141.2, 128.7, 128.3, 123.5, 119.7, 93.7 (quin-d, ^2J = 10.6 Hz, 0.7 Hz, C^3), 83.4 (quin, ^2J = 4.7 Hz, C^4), 82.3, 55.5 (quin, J = 4.0 Hz, C^2); ^{19}F NMR (376 MHz, $CDCl_3$): δ 83.8 (9 lines, A-part), 62.7 (dd, $^2J_{F,F}$ = 145.8 Hz, $^3J_{F,H}$ = 6.4 Hz, B_4-part); Anal. Calcd for $C_{10}H_8ClF_5OS$: C, 39.16; H, 2.63; Cl, 11.56. Found: C, 39.05; H, 2.61; Cl, 11.49.

Dimethyl *endo*-5-chloro-*exo*-6-(pentafluoro-λ^6-sulfanyl)-7-oxabicyclo[2.2.1]heptane-*exo*,*exo*-2,3-dicarboxylate (2b). 1.39 g (79%); white crystals, mp 70–71 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ 5.40 (s, 1H, H^1), 5.06 (d, $^3J_{4,5}$ = 5.1 Hz, 1H, H^4), 4.76 (t, $^3J_{5,4,6}$ = 5.1 Hz, 1H, H^5), 3.89 (m, $^3J_{6,F}$ = 5.7 Hz, $^3J_{6,5}$ = 5.1 Hz, 1H, H^6), 3.76 (d, $^3J_{2,3}$ = 9.6 Hz, 1H, H$^{2\text{ or }3}$), 3.74 (s, 3H), 3.73 (s, 3H), 3.17 (d, $^3J_{2,3}$ = 9.6 Hz, 1H, H$^{2\text{ or }3}$); ^{13}C NMR (50 MHz, $CDCl_3$): δ 170.4, 169.8, 93.4 (quin, ^2J = 12.6 Hz, C^6), 83.2 (quin, ^3J = 4.4 Hz, C^1), 81.9 (C^4), 58.1 (quin, ^3J = 3.9 Hz, C^5), 53.1, 53.0, 51.4, 45.4; ^{19}F NMR (188 MHz, $CDCl_3$): δ 81.7 (9 lines, A-part), 59.4 (dm, J = 146.3 Hz, B_4-part); HRMS (EI) for $[M - OCH_3]^+$ ($C_9H_9ClF_5O_4S$): calcd 342.9830, found 342.9831; for $[M - SF_5]^+$ ($C_{10}H_{12}ClO_5$): calcd 247.0373, found 247.0368.

***endo*-2-Chloro-*exo*,*exo*-5,6-bis(methoxymethyl)-*exo*-3-(pentafluoro-λ^6-sulfanyl)-7-oxa-bicyclo[2.2.1]heptane (2c).** 1.81 g (96%); white crystals, mp 51–52 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.96 (s, 1H, H^4), 4.67 (t, $^3J_{2,1,3}$ = 5.0 Hz, 1H, H^2), 4.50 (d, $^3J_{1,2}$ = 5.0 Hz, 1H, H^1), 3.91 (m, $^3J_{3,F}$ = 5.9 Hz, 1H, H^3), 3.40–3.21 (m, 4H, 2CH_2), 3.32 (s, 6H, 2CH_3), 2.87 (td, J = 9.1, 6.2 Hz, 1H), 2.26 (m, J = 9.1, 5.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 94.5 (quin, ^2J = 11.5 Hz, C^3), 83.5 (quin, ^3J = 5.2 Hz, C^4), 82.3 (C^1), 69.7 (CH_2), 69.6 (CH_2), 59.0 (OCH_3), 58.9 (OCH_3), 58.6 (quin, ^3J = 3.6 Hz, C^2), 45.9, 38.1; ^{19}F NMR (376 MHz, $CDCl_3$): δ 83.5 (9 lines, A-part), 59.61 (dd, J = 145.7, 5.9 Hz, B_4-part); Anal. Calcd for $C_{10}H_{16}ClF_5O_3S$: C, 34.64; H, 4.65; Cl, 10.22; S, 9.25. Found: C, 34.55; H 4.63; Cl, 10.16; S, 9.21.

***endo*-5-Chloro-*exo*-6-(pentafluoro-λ^6-sulfanyl)-7-oxabicyclo-[2.2.1]heptane-*exo*,*exo*-2,3-dicarbocyclic acid anhydride (2d).** 1.11 g (56%); white crystals, mp 89–91 °C; ^{1}H NMR (200 MHz, DMSO-d_6): δ 5.46 (s, 1H, H^1), 5.22 (d, $^3J_{4,5}$ = 4.8 Hz, 1H, H^4), 5.10–4.90 (m, 2H, H^{5,6}), 4.14 (d, $^3J_{2,3}$ = 7.5 Hz, 1H), 3.78 (d, $^3J_{2,3}$ = 7.4 Hz, 1H); ^{13}C NMR (50 MHz, DMSO-d_6): δ 172.2, 171.5, 93.3 (quin, ^2J = 9.8 Hz), 83.4 (d, ^3J = 4.3 Hz, C^1), 82.2 (C^4), 59.2 (d, ^3J = 4.3 Hz, C^5), 50.6, 45.2; ^{19}F NMR (188 MHz, DMSO-d_6): δ 85.2 (9 lines, A-part), 60.78 (dm, J = 151.5 Hz, B_4-part); Anal. Calcd for $C_8H_6ClF_5O_4S$: C, 29.24; H, 1.84; Cl, 10.79. Found: C 29.15; H 1.83; Cl 10.68.

General procedure for addition of CF_3I to 1a–c

A pressure glass ampoule (150 mL) fitted with a magnetic stirring bar was filled with a H_2O–CH_3CN solution (1 : 1, 40 mL), sodium dithionite (1.74 g, 8.5 mmol [85%]), $Na_3PO_4{\cdot}12H_2O$ (6.46 g, 17 mmol) and **1a** (1.23 g, 8.5 mmol). The ampoule was cooled to −78 °C and evacuated, and then trifluoroiodomethane (2.55 g, 13 mmol) was condensed in it. After warming up to ambient temperature the mixture was stirred for 40–48 h, then water was added (50 mL), the mixture was extracted with CH_2Cl_2 (4 × 15 mL), and the combined extracts were dried over Na_2SO_4. After evaporation of the solvent the pure product **3a** (2.6 g, 90%) was isolated by column chromatography (*n*-hexane–CH_2Cl_2 = 1/2).

Endo-2-iodo-*exo*-3-(trifluoromethyl)-1,2,3,4-tetrahydro-1,4-epoxynaphthalene (**3a**)

White crystals, mp 64–65 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (d, ^3J = 6.6 Hz, 1H), 7.39–7.26 (m, 3H), 5.47 (s, 1H, H^4), 5.39 (d, $^3J_{1,2}$ = 4.4 Hz, 1H, H^1), 4.21 (t, $^3J_{2,1,3}$ = 4.6 Hz, 1H, H^2), 2.48 (qd, $^3J_{3,F}$ = 8.7 Hz, $^3J_{3,2}$ = 4.6 Hz, 1H, H^3); ^{13}C NMR (101 MHz, $CDCl_3$): δ 142.9, 142.7, 128.3, 127.2, 126.5 (q, ^1J = 279.2 Hz, CF_3), 123.5, 119.0, 83.3 (C^1), 79.4 (q, ^3J = 2.4 Hz, C^4), 56.1 (q, ^2J = 27.8 Hz, C^3), 13.6 (q, ^3J = 1.2 Hz, C^2); ^{19}F NMR (376 MHz, $CDCl_3$): δ −68.52 (d, ^3J = 8.7 Hz); Anal. Calcd for $C_{11}H_8F_3IO$: C, 38.85; H, 2.37; I, 37.32. Found: C, 38.70; H, 2.36; I, 37.18.

Dimethyl *endo*-5-iodo-*exo*-6-(trifluoromethyl)-7-oxabicyclo-[2.2.1]heptane-*exo*,*exo*-2,3-dicarboxylate (3b). 2.81 g (81%); white crystals, mp 83–84 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.92 (d, $^3J_{4,5}$ = 4.7 Hz, 1H, H^4), 4.90 (s, 1H, H^1), 4.00 (dd, $^3J_{5,6}$ = 5.8 Hz, $^3J_{5,4}$ = 4.7 Hz, 1H, H^5), 3.91 (d, $^3J_{2,3}$ = 9.6 Hz, 1H), 3.71 (s, 3H, CH_3), 3.70 (s, 3H, CH_3), 3.05 (d, $^3J_{2,3}$ = 9.6 Hz, 1H), 2.54 (qd, $^3J_{6,F}$ = 8.3 Hz, $^3J_{6,5}$ = 5.8 Hz, 1H, H^6); ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.5, 169.8, 125.6 (q, ^1J = 279.0 Hz, CF_3), 82.3 (C^4), 78.7 (q, ^3J = 2.3 Hz, C^1), 57.8 (q, ^2J = 28.6 Hz, C^6), 52.6, 52.6, 51.5, 49.5, 15.2 (q, ^3J = 1.9 Hz, C^5); ^{19}F NMR (376 MHz, $CDCl_3$): δ −70.3 (d, ^3J = 8.3 Hz); HRMS (ESI) for $[M + Na]^+$ ($C_{11}H_{12}F_3INaO_5$): calcd 430.9574, found 430.9588.

***endo*-2-Iodo-*exo*,*exo*-5,6-bis(methoxymethyl)-*exo*-3-(tri-fluoromethyl)-7-oxabicyclo[2.2.1]heptane (3c).** 2.26 g (70%), *n*-hexane–CH_2Cl_2 = 1/5; white crystals, mp 41–42 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.44 (s, 1H, H^4), 4.33 (d, $^3J_{1,2}$ = 4.6 Hz, 1H, H^1), 3.92 (dd, $^3J_{2,3}$ = 5.8 Hz, $^3J_{2,1}$ = 4.6 Hz, 1H, H^2), 3.29 (s, 3H, CH_3), 3.27 (s, 3H, CH_3), 3.35–3.16 (m, 4H, 2CH_2), 2.99 (td, ^3J = 9.0, 6.3 Hz, 1H), 2.51 (qd, $^3J_{3,F}$ = 8.7 Hz, $^3J_{3,2}$ = 5.8 Hz, 1H, H^3), 2.13 (m, J = 9.2, 5.3 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 126.2 (q, ^1J = 278.9 Hz, CF_3), 82.8 (C^1), 79.2 (q, ^3J = 2.2 Hz, C^4), 70.2 (CH_2), 69.5 (CH_2), 58.9 (CH_3), 58.7 (CH_3), 57.8 (q, ^2J = 27.9 Hz, C^3), 46.0, 42.3, 17.3 (q, ^3J = 1.3 Hz, C^2); ^{19}F NMR (376 MHz, $CDCl_3$): δ −70.32 (d, ^3J = 8.7 Hz); HRMS (EI) for $[M]^+$ ($C_{11}H_{16}F_3IO_3$): calcd 380.0091, found 380.0097.

***exo*-2-Iodo-*exo*,*exo*-5,6-bis(methoxymethyl)-*exo*-3-(tri-fluoromethyl)-7-oxabicyclo[2.2.1]heptane (4c).** 0.16 g (5%), *n*-hexane–CH_2Cl_2 = 1/5; white crystals, mp 159–160 °C (sublime at >120 °C); ^{1}H NMR (401 MHz, $CDCl_3$): δ 4.70 (s, 1H, H^1), 4.63 (s, 1H, H^4), 4.10 (d, ^3J = 8.3 Hz, 1H, H^2), 3.31 (s, 6H, 2CH_3), 3.38–3.11 (m, 4H), 2.61 (qd, $^3J_{3,F}$ = 8.7 Hz, $^3J_{3,2}$ = 8.3 Hz, 1H, H^3), 2.15 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 124.2 (q, ^1J = 279.2 Hz, CF_3), 89.7 (C^1), 79.9 (d, ^3J = 2.1 Hz, C^4), 70.0 (CH_2), 69.9 (CH_2), 59.0 (2CH_3), 52.0 (q, ^2J = 27.6 Hz, C^3), 45.9, 45.5, 17.4 (d, ^3J = 1.2 Hz, C^2); ^{19}F NMR (376 MHz, $CDCl_3$): δ −64.6 (bs); HRMS (EI) for $[M]^+$ ($C_{11}H_{16}F_3IO_3$): calcd 380.0091, found 380.0076.

Dehydrohalogenation of 2a, c, 3a, c and 4c

2c (0.20 g, 0.58 mmol) was dissolved in DMSO (5 mL) and 5 equiv. of LiOH (0.069 g, 2.88 mmol) were added. The mixture

was stirred for 24 h at 50 °C. Water (50 mL) was added and the mixture was extracted with dichloromethane (5 × 10 mL); the combined extracts were washed with water (3 × 10 mL). After drying with sodium sulfate, the solvent was evaporated to obtain the crude product, which was purified by filtration through SiO_2 (CH_2Cl_2) giving **5c** (0.16 g, 92%).

Exo,*exo*-5,6-Bis(methoxymethyl)-2-(pentafluoro-λ^6-sulfanyl)-7-oxabicyclo-[2.2.1]hept-2-ene (**5c**)

White crystals, mp 38–39 °C; ^{1}H NMR (401 MHz, $CDCl_3$): δ 6.72 (m, J = 1.2 Hz, 1H, H^3), 5.04 (d, ^3J = 1.2 Hz, 1H, H^4), 4.96 (quin, $^4J_{1,F}$ = 1.2 Hz, 1H, H^1), 3.51 (dd, $^2J_{A,B}$ = 9.0 Hz, ^3J = 5.1 Hz, 1H, CH_2), 3.44 (dd, $^2J_{A,B}$ = 9.2 Hz, ^3J = 5.8 Hz, 1H, CH_2), 3.34 (s, 3H, OCH_3), 3.33 (s, 3H, OCH_3), 3.32–3.25 (m, 2H, CH_2), 2.25 (td, ^3J = 9.1, 5.8 Hz, 1H), 2.07 (ddd, ^3J = 10.2, 8.5, 5.1 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 160.2 (quind, $^2J_{2,Feq}$ = 18.7 Hz, $^2J_{2,Fax}$ = 2.0 Hz, C^2), 137.0 (quin, ^2J = 6.1 Hz, C^3), 81.6 (quin, ^3J = 3.4 Hz, C^1), 81.4 (C^4), 71.0 (OCH_3), 71.0 (OCH_3), 59.0 (OCH_2), 58.8 (OCH_2), 39.8 (C^{5,6}); ^{19}F NMR (376 MHz, $CDCl_3$): δ 82.32 (9 lines, A-part), 66.57 (d, J = 152.1 Hz, B_4-part); Anal. Calcd for $C_{10}H_{15}F_5O_3S$: C, 38.71; H, 4.87. Found: C, 38.59; H, 4.85.

2-(Pentafluoro-λ^6-sulfanyl)-1,4-dihydro-1,4-epoxynaphthalene (5a). 0.13 g (81%); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (m, 1H), 7.35–7.30 (m, 2H), 7.09 (m, 2H), 5.87 (s, 2H, H^{1,4}); ^{13}C NMR (101 MHz, $CDCl_3$): δ 169.5 (quin, ^2J = 19.6 Hz, C^2), 146.6, 145.8, 143.9 (quin, ^3J = 6.2 Hz), 126.4, 126.3, 121.5, 121.4, 83.5 (m, ^3J = 3.6 Hz, C^1), 83.1 (C^4); ^{19}F NMR (376 MHz, $CDCl_3$): δ 81.86 (9 lines, A-part), 66.24 (d, J = 152.9 Hz, B_4-part); Anal. Calcd for $C_{10}H_7F_5OS$: C, 44.45; H, 2.61. Found: C, 44.34; H, 2.60.

2-(Trifluoromethyl)-1,4-dihydro-1,4-epoxynaphthalene (6a). 0.10 g (84%); colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42–7.34 (m, 2H), 7.32 (m, 1H), 7.11–7.01 (m, 2H), 5.85 (m, 1H, H^1), 5.78 (s, 1H, H^4); ^{13}C NMR (101 MHz, $CDCl_3$): δ 147.1, 146.8, 146.4 (q, J = 1.3 Hz), 146.0 (q, $^3J_{3,F}$ = 4.9 Hz, C^3), 126.1, 126.0, 122.8 (q, ^1J = 267.7 Hz, CF_3), 121.2, 121.0, 83.1 (C^4), 81.2 (q, ^3J = 1.6 Hz, C^1); ^{19}F NMR (376 MHz, $CDCl_3$): δ −64.82 (s); Anal. Calcd for $C_{11}H_7F_3O$: C, 62.27; H, 3.33. Found: C, 62.12; H, 3.32.

***exo*,*exo*-5,6-Bis(methoxymethyl)-2-(trifluoromethyl)-7-oxabicyclo[2.2.1]hept-2-ene (6c).** 0.13 g (89%); colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.76 (m, J = 2.3 Hz, 1H, H^3), 4.97 (s, 1H, H^1), 4.92 (m, 1H, H^4), 3.51 (dd, $^1J_{A,B}$ = 8.9 Hz, ^3J = 5.0 Hz, 1H, CH_2), 3.45 (dd, $^1J_{A,B}$ = 9.1 Hz, ^3J = 5.7 Hz, 1H, CH_2), 3.36 (s, 3H, OCH_3), 3.35 (s, 3H, OCH_3), 3.38–3.25 (m, 2H, CH_2), 2.07 (ddd, ^3J = 8.7 Hz, 5.7 Hz, 1H), 2.00 (ddd, ^3J = 9.9 Hz, 8.7 Hz, 5.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 139.1 (q, ^2J = 35.4 Hz, C^2), 138.8 (q, ^3J = 4.8 Hz, C^3), 122.0 (q, ^1J = 267.9 Hz, CF_3), 81.6 (C^4), 79.3 (q, ^3J = 1.4 Hz, C^1), 71.2 (OCH_3), 71.1 (OCH_3), 58.9 (CH_2), 58.8 (CH_2), 40.0 (C^5), 39.8 (q, J = 1.3 Hz, C^6); ^{19}F NMR (376 MHz, $CDCl_3$): δ −63.6 (s); HRMS (ESI) for $[M]^+$ ($C_{11}H_{15}F_3NaO_3$): calcd 275.0866, found 275.0867.

Dimethyl 4-(trifluoromethyl)phthalate (7b).[34] **3b** (0.20 g, 0.49 mmol) was dissolved in DMSO (5 mL) and 5 equiv. of K_2CO_3 (0.34 g, 2.45 mmol) were added. The mixture was stirred for 12 h at 60 °C. 100 mL of water was added and the mixture was extracted with dichloromethane (5 × 10 mL). After drying with sodium sulfate, the solvent was evaporated to obtain the crude product, which was purified by column chromatography (pentane–dichloromethane = 10/1) yielding **7b** (0.10 g, 78%) as a colourless liquid. ^{1}H NMR (401 MHz, $CDCl_3$): δ 8.02 (s, 1H), 7.80 (d, J = 0.9 Hz, 2H), 3.93 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 167.2, 166.4, 135.7 (q, ^4J = 1.1 Hz), 133.1 (q, ^2J = 33.5 Hz, C^4), 132.2, 129.4, 128.2 (q, ^3J = 3.7 Hz), 126.3 (q, ^3J = 3.8 Hz), 123.2 (d, ^1J = 272.8 Hz, CF_3), 53.1, 53.1; ^{19}F NMR (377 MHz, $CDCl_3$): δ −63.04 (s).

Dimethyl *endo*-5-iodo-*exo*-6-(trifluoromethyl)-7-oxabicyclo-[2.2.1]heptane-*endo*-2-*exo*-3-dicarboxylate (8). 3b (0.10 g, 0.25 mmol) was dissolved in dichloromethane (2 mL), and 1.2 eq. of DBU (0.046 g, 0.30 mmol) were added at 0 °C. The reaction mixture was stirred for 12 h at rt. The reaction mixture was diluted with dichloromethane (5 mL) and washed with water (3 × 3 mL). After drying with sodium sulfate the solvent was evaporated to obtain the crude product, which was purified by filtration through silica gel giving **8** (0.072 g, 72%). White crystals, mp 68–71 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.86 (d, $^3J_{1,2}$ = 5.0 Hz, 1H, H^1), 4.76 (d, $^3J_{4,5}$ = 5.5 Hz, 1H, H^4), 4.05 (dd, ^3J = 6.2, 5.5 Hz, 1H, H^5), 3.90 (d, $^3J_{3,2}$ = 6.0 Hz, 1H, H^3), 3.78 (s, 3H, CH_3), 3.76 (s, 3H, CH_3), 3.55 (dd, ^3J = 6.0, 5.0 Hz, 1H, H^2), 2.65 (qd, $^3J_{6,F}$ = 8.6 Hz, $^3J_{6,5}$ = 6.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 171.9, 169.6, 125.9 (q, ^1J = 278.9 Hz, CF_3), 84.6, 78.3 (q, ^3J = 2.3 Hz, C^1), 53.6 (q, ^2J = 28.8 Hz, C^6), 53.0, 52.9, 51.1, 48.2, 15.5 (d, ^3J = 1.4 Hz, C^5); ^{19}F NMR (376 MHz, $CDCl_3$): δ −70.3 (d, ^3J = 8.5 Hz); HRMS (ESI) for $[M + Na]^+$ ($C_{11}H_{12}F_3INaO_5$): calcd 430.9574, found 430.9588.

Dimethyl 5-chloro-3-oxatricyclo[2.2.1.0^{2,6}]heptane-1,7-dicarboxylate (9). 2b (0.10 g, 0.27 mmol) was dissolved in dichloromethane (2 mL), and then 2 equiv. of DBU (0.082 g, 0.54 mmol) were added at 0 °C. The reaction mixture was stirred for 12 h at rt. The reaction mixture was diluted with 10 mL of dichloromethane, and washed with water (3 × 2 mL). After drying with sodium sulfate the solvent was evaporated to obtain the crude product, which was purified by filtration through silica gel (CH_2Cl_2) giving **9** (0.035 g, 53%). Colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.66 (d, J = 3.9 Hz, 1H, H^2), 4.34 (m, 1H, H^4), 4.01 (t, J = 2.1 Hz, 1H, H^5), 3.73 (s, 3H, OCH_3), 3.71 (s, 3H, OCH_3), 3.67 (s, 1H, H^7), 2.35 (m, 1H, H^6); ^{13}C NMR (101 MHz, $CDCl_3$): δ 169.8, 169.0, 78.0 (C^4), 61.4 (C^2), 59.3 (C^5), 52.4 (OCH_3), 52.29 (OCH_3), 46.7 (C^7), 29.8 (C^1), 29.2 (C^6); HRMS (ESI) for $[M + Na]^+$ ($C_{10}H_{11}ClNaO_5$): calcd 269.0187, found 269.0188.

The preparation of R_F-naphthols 10–11a. 5a (0.13 g, 0.48 mmol) was dissolved in a mixture of methanol and hydrochloric acid (37% aq.) (3/1 mL). The reaction mixture was stirred for 70 h at 90 °C. Water (20 mL) was added to the reaction mixture and the mixture was extracted with dichloromethane (5 × 5 mL), and washed with water (3 × 3 mL). After drying with sodium sulfate the solvent was evaporated. The crude product was purified by column chromatography (*n*-hexane–CH_2Cl_2 = 10/1) yielding **10a** (0.083 g, 64%).

2-(Pentafluoro-λ^6-sulfanyl)-1-naphthol (10a). White crystals, mp 69–71 °C; ^{1}H NMR (401 MHz, $CDCl_3$): δ 8.42 (d, ^3J = 8.3 Hz,

1H), 7.79 (d, ^3J = 7.9 Hz, 1H), 7.67–7.51 (m, 3H), 7.40 (d, ^3J = 9.3 Hz, 1H), 6.77 (quin, J = 4.9 Hz, 1H, OH); ^{13}C NMR (101 MHz, $CDCl_3$): δ 147.1 (quin, ^3J = 2.1 Hz, C^1), 135.9–134.8 (quin, ^2J = 13.1 Hz, C^2), 135.3, 129.2, 127.3, 126.7, 125.8, 124.0, 122.9 (quin, ^3J = 5.0 Hz, C^3), 120.1; ^{19}F NMR (377 MHz, $CDCl_3$): δ 86.6 (9 lines, A-part), 67.1 (dm, J = 148.8 Hz, B_4-part); IR (KBr) ν_{max} 3633, 2964, 1633, 1581, 1503, 1461, 1412; HRMS (ESI) for $[M - H]^-$ ($C_{10}H_6F_5OS$): calcd 269.0066, found 269.0065.

2-(Trifluoromethyl)-1-naphthol (11a). Pale yellow crystals, mp 37–38 °C; 0.082 g (41%, from 0.20 g, 0.94 mmol of **6a**); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.34 (d, ^3J = 7.9 Hz, 1H), 7.82 (dd, ^3J = 7.4 Hz, ^4J = 1.3 Hz, 1H), 7.59 (m, 2H), 7.47 (m, 2H), 6.32 (q, J = 5.1 Hz, 1H, OH); ^{13}C NMR (101 MHz, $CDCl_3$): δ 150.7 (q, ^3J = 2.5 Hz, C^1), 136.2, 128.7, 127.7, 126.5, 125.5 (q, ^1J = 272.0 Hz, CF_3), 124.9, 122.9, 121.7 (q, ^3J = 4.2 Hz, C^3), 120.8, 109.1 (q, ^2J = 29.1 Hz, C^2); ^{19}F NMR (377 MHz, $CDCl_3$): δ −59.0 (d, J = 5.0 Hz); Anal. Calcd for $C_{11}H_7F_3O$: C, 62.27; H, 3.33. Found: C, 62.08; H, 3.32.

The spectral data of methyl 4-hydroxy-2-naphthoate (**12**) and 1-hydroxy-2-naphthoate (**12′**) correspond with the literature data.[35]

4-(Pentafluoro-λ^6-sulfanyl)benzyl acetate (13). 5c (0.1 g, 0.32 mmol) was dissolved in a mixture of AcOH and H_2SO_4 (98%) (5/1 mL). The reaction mixture was stirred for 24 h at 100 °C. Water (40 mL) was added to the reaction mixture and the mixture was extracted with dichloromethane (5 × 8 mL), and washed with water (4 × 3 mL). After drying with sodium sulfate the solvent was evaporated. The crude product was purified by column chromatography (*n*-hexane–CH_2Cl_2 = 1/1) yielding **13** (0.017 g, 19%, only *ca.* 82% of purity by NMR). Pale yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (dm, J = 8.3 Hz, 2H), 7.44 (dm, J = 8.3 Hz, 2H), 5.14 (s, 2H, CH_2), 2.12 (s, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.7, 147.0 (m), 139.9, 128.1, 126.3 (quin, J = 4.6 Hz), 64.9, 20.9; ^{19}F NMR (376 MHz, $CDCl_3$): δ 84.30 (tt, J = 154.6, 147.4 Hz), 62.93 (d, J = 150.0 Hz).

5-(Pentafluoro-λ^6-sulfanyl)-1,3-dihydro-2-benzofuran (14c). 3 mL of hydrochloric acid (37% aq.) and **5c** (0.2 g, 0.64 mmol) were mixed in a 10 mL flask. The reaction mixture was stirred *ca.* 90 h at 100 °C. Water (40 mL) was added to the reaction mixture and the mixture was extracted with dichloromethane (5 × 8 mL), and washed with water (4 × 3 mL). After drying with sodium sulfate the solvent was evaporated. The reaction mixture was separated by column chromatography (CH_2Cl_2) giving **14c** (0.089 g, 56%) and **15** (0.012 g, 6%). **14c**: white crystals, mp 89–90 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (dd, ^3J = 8.3 Hz, ^4J = 1.8 Hz, 1H), 7.62 (d, ^4J = 1.8 Hz, 1H), 7.31 (d, J = 8.3 Hz, 1H), 5.14 (s, 4H, CH_2); ^{13}C NMR (101 MHz, $CDCl_3$): δ 153.6 (qd, $^2J_{5,Feq}$ = 17.3 Hz, $^2J_{5,Fax}$ = 1.2 Hz), 142.9, 140.2, 125.4 (q, ^3J = 4.7 Hz), 121.2, 119.1 (q, ^3J = 4.6 Hz), 73.3, 73.2; ^{19}F NMR (376 MHz, $CDCl_3$): δ 84.8 (9 lines, A-part), 63.7 (d, J = 150.0 Hz, B_4-part); Anal. Calc. for $C_8H_7F_5OS$: C, 39.03; H, 2.87. Found: C, 38.92; H, 2.86.

5,6-Bis(chloromethyl)-2-(pentafluoro-λ^6-sulfanyl)-7-oxabicyclo-[2.2.1]hept-2-ene (15). Pale yellow oil; ^{1}H NMR (400 MHz, C_6D_6): δ 5.86 (m, 1H, H^3), 4.54 (d, J = 1.3 Hz, 1H, H^1), 3.40 (m, 1H, H^4), 3.10 (dd, $^2J_{AB}$ = 10.2 Hz, ^3J = 6.1 Hz, 1H, CH_2), 2.69 (dd, $^2J_{AB}$ = 11.1 Hz, ^3J = 8.0 Hz, 1H, CH_2), 2.65–2.51 (m, 2H, CH_2), 2.28 (t, J = 8.0 Hz, 1H), 1.86 (dd, J = 6.1, 1.6 Hz, 1H); ^{13}C NMR (101 MHz, C_6D_6): δ 156.9 (quin, ^2J = 13.5 Hz, C^2), 130.6 (quin, ^3J = 5.4 Hz, C^3), 74.8 (quin, ^3J = 3.0 Hz, C^1), 66.9 (CH_2), 56.3 (C^4), 45.2, 43.3, 42.4 (CH_2); ^{19}F NMR (376 MHz, $CDCl_3$): δ 82.1 (9 lines, A-part), 59.1 (d, J = 150.2 Hz, B_4-part); HRMS (CI) for $[M - OH]^+$ ($C_8H_8Cl_2F_5S$): calc. 300.9644, found 300.9646. HRMS (CI) for $[M - F]^+$ ($C_8H_9Cl_2F_4S$): calc. 298.9687, found 298.9694.

5-(Trifluoromethyl)-1,3,3a,4,7,7a-hexahydro-4,7-epoxy-2-benzofuran (17). 6c (0.15 g, 0.59 mmol) was dissolved in 5 mL of trifluoroacetic acid. The reaction mixture was refluxed 3 h. TFA was evaporated, the reaction mixture was dissolved in 10 mL of CH_2Cl_2, and washed with water (2 × 2 mL). After drying with sodium sulfate the solvent was evaporated. The crude product was purified by filtration through silica gel (pentane–CH_2Cl_2 = 1/1) giving 17 (0.093 g, 76%). Colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.81 (dq, $^3J_{6,F}$ = 4.3 Hz, ^3J = 2.3 Hz, 1H, H^6), 4.89 (s, 1H), 4.87 (s, 1H), 3.94 (ddd, J = 9.3, 7.4, 3.2 Hz, 2H), 3.64 (ddd, J = 9.2, 4.8, 2.5 Hz, 2H), 2.61 (dtd, J = 26.6, 7.7, 4.9 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 140.8 (q, ^2J = 35.8 Hz, C^5), 139.9 (q, ^3J = 4.8 Hz, C^6), 122.1 (q, J = 267.9 Hz, CF_3), 82.9, 80.6 (q, ^3J = 1.3 Hz, C^4), 70.9, 70.8, 47.7, 47.4 (q, ^4J = 1.4 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ −63.8 (m); Anal. Calc. for $C_9H_9F_3O_2$: C, 52.43; H, 4.40. Found: C, 52.29; H, 4.38.

Acknowledgements

This work was supported by the Deutsche Forschungsgemeinschaft (436 UKR 113/99/0-1). AAF is grateful to the University of Giessen (Germany) and the Institute of Applied System Analysis (Kiev, Ukraine) for computing facilities.

Notes and references

1 (*a*) J. Nie, H.-C. Guo, D. Cahard and J.-A. Ma, *Chem. Rev.*, 2010, **111**, 455–529; (*b*) D. O'Hagan, *J. Fluorine Chem.*, 2010, **131**, 1071–1081; (*c*) O. A. Tomashenko and V. V. Grushin, *Chem. Rev.*, 2011, **111**, 4475–4521; (*d*) S. Purser, P. R. Moore, S. Swallow and V. Gouverneur, *Chem. Soc. Rev.*, 2008, **37**, 320–330; (*e*) G. K. S. Prakash and S. Chacko, *Curr. Opin. Drug Discovery Dev.*, 2008, **11**, 793–802; (*f*) A. T. Parsons and S. L. Buchwald, *Nature*, 2011, **480**, 184–185; (*g*) K. Müller, C. Faeh and F. Diederich, *Science*, 2007, **317**, 1881–1886; (*h*) J.-A. Ma and D. Cahard, *J. Fluorine Chem.*, 2007, **128**, 975–996.

2 (*a*) S. Altomonte and M. Zanda, *J. Fluorine Chem.*, 2012, **143**, 57–93; (*b*) P. J. Crowley, G. Mitchell, R. Salmon and P. A. Worthington, *Chimia*, 2004, **58**, 138–142; (*c*) G. L. Gard, *Chim. Oggi*, 2009, **27**, 10–13; (*d*) P. Kirsch and G. V. Röschenthaler, in *Current Fluoroorganic Chemistry – New Synthetic Directions, Technologies, Materials, and Biological Applications*, ed. V. A. Soloshonok, K. Mikami,

T. Yamazaki, J. T. Welch and J. F. Honek, ACS Press, Washington 9492007, pp. 221–243; (*e*) R. W. Winter, R. A. Dodean and G. L. Gard, in *ACS Symposium Series, 911: Fluorine-Containing Synthons*, ed. V. A. Soloshonok, American Chemical Society, Washington, DC2005, pp. 87–118; (*f*) G. S. Lal and R. G. Syvret, *Chim. Oggi*, 2008, **26**, 26–27; (*g*) P. Kirsch, J. T. Binder, E. Lork and G.-V. Röschenthaler, *J. Fluorine Chem.*, 2006, **127**, 610–619.

3 (*a*) P. Kirsch and A. Hahn, *Eur. J. Org. Chem.*, 2005, 3095–3100; (*b*) M. V. Ponomarenko, N. Kalinovich, Y. A. Serguchev, M. Bremer and G.-V. Röschenthaler, *J. Fluorine Chem.*, 2012, **135**, 68–74.

4 (*a*) J. T. Welch and D. S. Lim, *Bioorg. Med. Chem.*, 2007, **15**, 6659–6666; (*b*) T. Mo, X. Mi, E. E. Milner, G. S. Dow and P. Wipf, *Tetrahedron Lett.*, 2010, **51**, 5137–5140; (*c*) B. Stump, C. Eberle, W. B. Schweizer, M. Kaiser, R. Brun, R. L. Krauth-Siegel, D. Lentz and F. Diederich, *ChemBioChem*, 2009, **10**, 79–83; (*d*) P. Wipf, T. Mo, S. J. Geib, D. Caridha, G. S. Dow, L. Gerena, N. Roncal and E. E. Milner, *Org. Biomol. Chem.*, 2009, **7**, 4163–4165; (*e*) P. W. Chia, S. C. Brennan, A. M. Z. Slawin, D. Riccardi and D. O'Hagan, *Org. Biomol. Chem.*, 2012, **10**, 7922–7927; (*f*) J. M. Coteron, M. Marco, J. Esquivias, X. Deng, K. L. White, J. White, M. Koltun, F. El Mazouni, S. Kokkonda, K. Katneni, R. Bhamidipati, D. M. Shackleford, I. Angulo-Barturen, S. B. Ferrer, M. B. Jiménez-Díaz, F.-J. Gamo, E. J. Goldsmith, W. N. Charman, I. Bathurst, D. Floyd, D. Matthews, J. N. Burrows, P. K. Rathod, S. A. Charman and M. A. Phillips, *J. Med. Chem.*, 2011, **54**, 5540–5561.

5 (*a*) H. L. Roberts, *J. Chem. Soc.*, 1962, 3183–3185; (*b*) W. A. Sheppard, *J. Am. Chem. Soc.*, 1962, **84**, 3064–3072.

6 (*a*) R. D. Chambers and R. C. H. Spink, *J. Chem. Soc., Chem. Commun.*, 1999, 883–884; (*b*) R. D. Bowden, P. J. Comina, M. P. Greenhall, B. M. Kariuki, A. Loveday and D. Philp, *Tetrahedron*, 2000, **56**, 3399–3408.

7 T. Umemoto, L. M. Garrick and N. Saito, *Beilstein J. Org. Chem.*, 2012, **8**, 461–471.

8 (*a*) P. Beier, T. Pastýříková and G. Iakobson, *J. Org. Chem.*, 2011, **76**, 4781–4786; (*b*) T. Pastýříková, G. Iakobson, N. Vida, R. Pohl and P. Beier, *Eur. J. Org. Chem.*, 2012, 2123–2126; (*c*) N. Vida and P. Beier, *J. Fluorine Chem.*, 2012, **143**, 130–134; (*d*) A. Frischmuth, A. Unsinn, K. Groll, H. Stadtmüller and P. Knochel, *Chem.–Eur. J.*, 2012, **18**, 10234–10238.

9 (*a*) F. W. Hoover and D. D. Coffman, *J. Org. Chem.*, 1964, **29**, 3567–3570; (*b*) T. A. Sergeeva and W. R. Dolbier Jr., *Org. Lett.*, 2004, **6**, 2417–2419; (*c*) R. W. Winter and G. L. Gard, *J. Fluorine Chem.*, 2004, **125**, 549–552.

10 (*a*) M. Lautens, *Synlett*, 1993, 177–185; (*b*) D. K. Rayabarapu and C.-H. Cheng, *Acc. Chem. Res.*, 2007, **40**, 971–983; (*c*) M. Lautens, K. Fagnou and S. Hiebert, *Acc. Chem. Res.*, 2003, **36**, 48–58; (*d*) S. Woo and B. A. Keay, *Synthesis*, 1996, 669–686.

11 (*a*) M. Lautens and S. Hiebert, *J. Am. Chem. Soc.*, 2004, **126**, 1437–1447; (*b*) M. Lautens and T. Rovis, *Tetrahedron*, 1998, **54**, 1107–1116; (*c*) K. Villeneuve and W. Tam, *J. Am. Chem. Soc.*, 2006, **128**, 3514–3515; (*d*) J. Zhu, G. C. Tsui and M. Lautens, *Angew. Chem., Int. Ed.*, 2012, **51**, 12353–12356; (*e*) T. Yano, T. Fujishima and R. Irie, *Synthesis*, 2010, 818–822; (*f*) I. B. Masesane and P. G. Steel, *Tetrahedron Lett.*, 2004, **45**, 5007–5009; (*g*) S. Ito, T. Itoh and M. Nakamura, *Angew. Chem., Int. Ed.*, 2011, **50**, 454–457.

12 (*a*) M. Ballantine, M. L. Menard and W. Tam, *J. Org. Chem.*, 2009, **74**, 7570–7573; (*b*) C.-L. Chen and S. F. Martin, *J. Org. Chem.*, 2006, **71**, 4810–4817; (*c*) K.-Y. Jung and M. Koreeda, *J. Org. Chem.*, 1989, **54**, 5667–5675; (*d*) E. Masson and M. Schlosser, *Eur. J. Org. Chem.*, 2005, 4401–4405; (*e*) F. Bailly, F. Cottet and M. Schlosser, *Synthesis*, 2005, 791–797; (*f*) M. Schlosser and E. Castagnetti, *Eur. J. Org. Chem.*, 2001, 3991–3997; (*g*) A. Padwa, M. Dimitroff, A. G. Waterson and T. Wu, *J. Org. Chem.*, 1997, **62**, 4088–4096.

13 (*a*) K. I. Booker-Milburn, P. Hirst, J. P. H. Charmant and L. H. J. Taylor, *Angew. Chem., Int. Ed.*, 2003, **42**, 1642–1644; (*b*) M. Hamada, Y. Inami, Y. Nagai, T. Higashi, M. Shoji, S. Ogawa, K. Umezawa and T. Sugai, *Tetrahedron: Asymmetry*, 2009, **20**, 2105–2111; (*c*) A. Venkatram, T. Colley, J. DeRuiter and F. Smith, *J. Heterocycl. Chem.*, 2005, **42**, 297–301; (*d*) J. Chola and I. B. Masesane, *Tetrahedron Lett.*, 2008, **49**, 5680–5682; (*e*) S. Borthwick, W. Dohle, P. R. Hirst and K. I. Booker-Milburn, *Tetrahedron Lett.*, 2006, **47**, 7205–7208; (*f*) A. Aljarilla, M. C. Murcia and J. Plumet, *Synlett*, 2006, 831–832; (*g*) A. Baran, C. Kazaz, H. Seçen and Y. Sütbeyaz, *Tetrahedron*, 2003, **59**, 3643–3648; (*h*) K. Villeneuve and W. Tam, *Organometallics*, 2007, **26**, 6082–6090; (*i*) A. Padwa and Q. Wang, *J. Org. Chem.*, 2006, **71**, 7391–7402; (*j*) A. Aljarilla, M. C. Murcia, A. G. Csákÿ and J. Plumet, *Eur. J. Org. Chem.*, 2009, 822–832; (*k*) D. B. Millward, G. Sammis and R. M. Waymouth, *J. Org. Chem.*, 2000, **65**, 3902–3909; (*l*) M. Nakamura, K. Matsuo, T. Inoue and E. Nakamura, *Org. Lett.*, 2003, **5**, 1373–1375; (*m*) A. Baran, C. Kazaz and H. Seçen, *Tetrahedron*, 2004, **60**, 861–866; (*n*) D. K. Rayabarapu, P. Shukla and C.-H. Cheng, *Org. Lett.*, 2003, **5**, 4903–4906.

14 (*a*) O. Arjona, R. Fernandez de la Pradilla, J. Plumet and A. Viso, *J. Org. Chem.*, 1992, **57**, 772–774; (*b*) O. Arjona, R. Fernandez de la Pradilla, L. García, A. Mallo and J. Plumet, *J. Chem. Soc., Perkin Trans. 2*, 1989, 1315–1318; (*c*) K. Kraehenbuehl and P. Vogel, *Tetrahedron Lett.*, 1995, **36**, 8595–8598.

15 W. R. Dolbier Jr., A. Mitani, W. Xu and I. Ghiviriga, *Org. Lett.*, 2006, **8**, 5573–5575.

16 W. R. Dolbier Jr., A. Mitani and R. D. Warren, *Tetrahedron Lett.*, 2007, **48**, 1325–1326.

17 D. Peña, A. Cobas, D. Pérez and E. Guitián, *Synthesis*, 2002, 1454–1458.

18 S. Aït-Mohand and W. R. Dolbier Jr., *Org. Lett.*, 2002, **4**, 3013–3015.

19 J. Ignatowska and W. Dmowski, *J. Fluorine Chem.*, 2007, **128**, 997–1006.

20 D. Lentz and K. Seppelt, in *Chemistry of Hypervalent Compounds*, ed. K. Akiba, Wiley-VCH, 1999, pp. 295–325.
21 (*a*) K.-H. Chung, H. G. Lee, I.-Y. Choi and J.-R. Choi, *J. Org. Chem.*, 2001, **66**, 5937–5939; (*b*) F. Brion, *Tetrahedron Lett.*, 1982, **23**, 5299–5302.
22 (*a*) W. R. Dolbier Jr. and Z. Zheng, *J. Org. Chem.*, 2009, **74**, 5626–5628; (*b*) Y. Huang, G. L. Gard and J. M. Shreeve, *Tetrahedron Lett.*, 2010, **51**, 6951–6954.
23 J. Duan, L. H. Zhang and W. R. Dolbier Jr., *Synlett*, 1999, 1245–1246.
24 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, J. J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *GAUSSIAN 09*.
25 (*a*) J. A. K. Howard, V. J. Hoy, D. O'Hagan and G. T. Smith, *Tetrahedron*, 1996, **52**, 12613–12622; (*b*) H.-J. Schneider, *Chem. Sci.*, 2012, **3**, 1381.
26 D. O'Hagan, *Chem. Soc. Rev.*, 2008, **37**, 308–319.
27 H. Takemura, M. Kaneko, K. Sako and T. Iwanaga, *New J. Chem.*, 2009, **33**, 2004–2006.
28 (*a*) P. R. Savoie, S. Higashiya, J.-H. Lin, D. V. Wagle and J. T. Welch, *J. Fluorine Chem.*, 2012, **143**, 281–286; (*b*) P. R. Savoie, J. M. Welch, S. Higashiya and J. T. Welch, *J. Fluorine Chem.*, 2013, **148**, 1–5.
29 (*a*) S. Fung, N. A. Abraham, F. Bellini and K. Sestanj, *Can. J. Chem.*, 1983, **61**, 368–371; (*b*) A. G. Sergeev, T. Schulz, C. Torborg, A. Spannenberg, H. Neumann and M. Beller, *Angew. Chem., Int. Ed.*, 2009, **48**, 7595–7599; (*c*) T. Umemoto and S. Ishihara, *J. Am. Chem. Soc.*, 1993, **115**, 2156–2164; (*d*) T. R. Wu, L. Shen and J. M. Chong, *Org. Lett.*, 2004, **6**, 2701–2704.
30 (*a*) E. L. Nava, A. Jesih and E. Goreshnik, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2008, **64**, o416; (*b*) C. Zarantonello, A. Guerrato, E. Ugel, R. Bertani, F. Benetollo, R. Milani, A. Venzo and A. Zaggia, *J. Fluorine Chem.*, 2007, **128**, 1449–1453; (*c*) P. Kirsch, M. Bremer, M. Heckmeier and K. Tarumi, *Angew. Chem., Int. Ed.*, 1999, **38**, 1989–1992.
31 A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441–451.
32 G. M. Sheldrick, *Program for empirical X-ray absorption correction*, Bruker-Nonius, 1990.
33 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, 64.
34 J.-N. Volle and M. Schlosser, *Eur. J. Org. Chem.*, 2002, 1490–1492.
35 (*a*) E. Oishi and E. Hayashi, *Yakugaku Zasshi*, 1983, **103**, 34–42; (*b*) S. W. Youn, B. S. Kim and A. R. Jagdale, *J. Am. Chem. Soc.*, 2012, **134**, 11308–11311.

