CHEMISTRY
A EUROPEAN JOURNAL

FULL PAPER

DOI: 10.1002/chem.201203315

Design and Synthesis of a New Family of Fluorinated Liquid Crystals

Valentine G. Nenajdenko,*[a] Aleksey A. Goldberg,[a] Vasily M. Muzalevskiy,[a] Elizabeth S. Balenkova,[a] and Aleksey V. Shastin[b]

Abstract: A convenient and simple three-step pathway to the new family of CF_2CF_2S-bridged alkanes and CF_2S-, CF_2O-bridged alkenes and alkynes was elaborated by using catalytic olefination reaction as a key step of the synthetic sequence. The obtained compounds revealed attractive liquid crystalline characteristics.

Keywords: 1,2-dibromotetrafluoroethane · cross-coupling · liquid crystals · nucleophilic substitution · olefination

Introduction

Invented in the 1960s by the Radio Corporation of America (RCA), liquid-crystal displays (LCD) have become a very important part of modern society. One can hardly imagine a life without numerous electronic devices with LCD's, which are an attribute of the present day. Fluorinated compounds dominate among liquid crystalline materials used currently for active LCD matrix due to optimal values of the dielectric anisotropy ($\Delta\varepsilon$), melting and clearing points, mesophase sequence, and solubility (Figure 1).[1] The significant advantages of fluorinated liquid-crystals are their improved reliability and enhanced thermo- and photostabilities. At the same time, there are some upsetting drawbacks of these compounds such as relatively high price, quite complicated synthesis, and the lack of general methodology of their preparation. The last circumstance is the most annoying, because it makes the synthesis of each new molecule to be a challenge. Therefore, a development of new efficient synthetic pathways to fluorinated liquid crystals starting form cheap and readily available starting materials is a very important task. Moreover, rather desirable are such synthetic pathways that enable the preparation of target molecules in short and effective manner giving diversity of final compounds for subsequent screening of liquid-crystal properties.

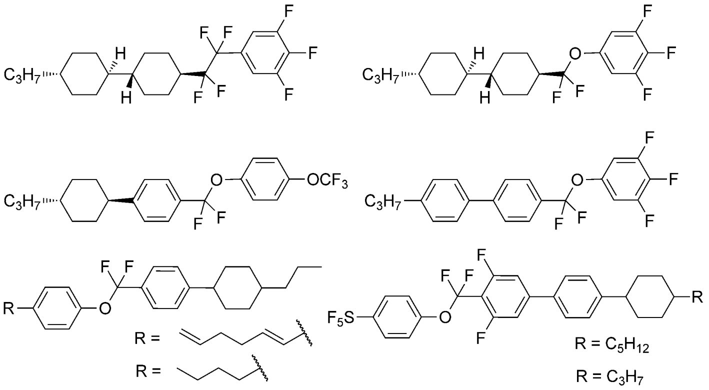


Figure 1. Commercial calamitic liquid-crystals.

1,2-Dibromotetrafluoroethane is very cheap fluorinated building block (120 Euro kg^{-1} in laboratory scale). Due to the presence of quite reactive bromines, it can be involved in a number of widely used reactions such as, for example, radical and nucleophilic substitution, bromination of carbanions, and others. Consequently, on the basis of $BrCF_2CF_2Br$, new simple and economical pathways towards compounds having such interesting fluorinated fragments as $CH_2CF_2CF_2X$ and CF_2X (X = O, N, S) can be developed. These compounds could be very attractive liquid-crystal candidates, because such fluorinated fragments as CF_2CF_2 and CF_2O bridges have already shown good liquid-crystalline properties.[2]

In this article we propose a new divergent approach (diversity-oriented synthesis) to a family of new liquid-crystals based on use of 1,2-dibromotetrafluoroethane. It should be noted that the proposed synthetic approach opens the possibility for screening of new liquid-crystalline compounds by tuning their properties due to the possibility of effective variation of substituents at the final step of synthetic sequence. Despite the progress in the field of prediction of the properties of liquid crystals, it is still extremely complicated task and empirical screening is the most successful way in this field. Therefore the effectiveness of screening and the effectiveness of synthetic construction of new liquid-crystalline compounds are most crucial steps for the progress in this field.

---

[a] Prof. Dr. V. G. Nenajdenko, Dr. A. A. Goldberg,
Dr. V. M. Muzalevskiy, Prof. Dr. E. S. Balenkova
Department of Chemistry
Moscow State University
Leninskie Gory
Moscow 119992 (Russia)
Fax: (+)7-495-9328846
E-mail: nen@acylium.chem.msu.ru

[b] Dr. A. V. Shastin
Institute of Problems of Chemical Physics
Chernogolovka, Moscow Region 142432 (Russia)

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201203315.

Results and Discussion

Currently, the strategy for design of liquid crystalline compounds dictates some basic structural requirements to the molecules that are possible calamitic liquid-crystal candidates.[3] As a rough approximation, the molecule should have a rod-like structure with a reasonable length, typically containing core units (A and B) such as *trans*-1,4-disubstituted cyclohexane, 1,4-disubstituted benzene (often 1,4′-biaryl), other aromatic or heteroaromatic rings, substituted by lateral groups M, N and linked by small groups (Y) like ester, imine, ethenyl, ethynyl, methyleneoxy, and dimethylene functions. (Figure 2) However, the linking groups are not always presented and a direct connection with a single bond can be used instead of any linkage. The main core units A and B should be linked with some terminal units RX and ZR′, which are usually moderately long linear alkyl chains or small substituents (e.g., fluoro, chloro, bromo, trifluoromethyl, SF_5, cyano, and nitro).

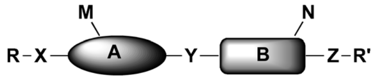
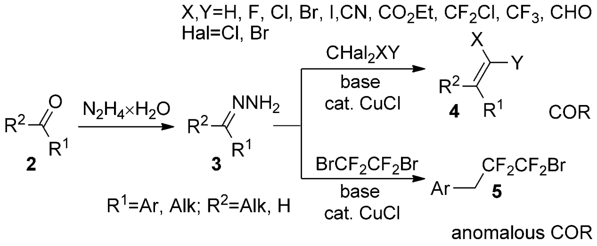


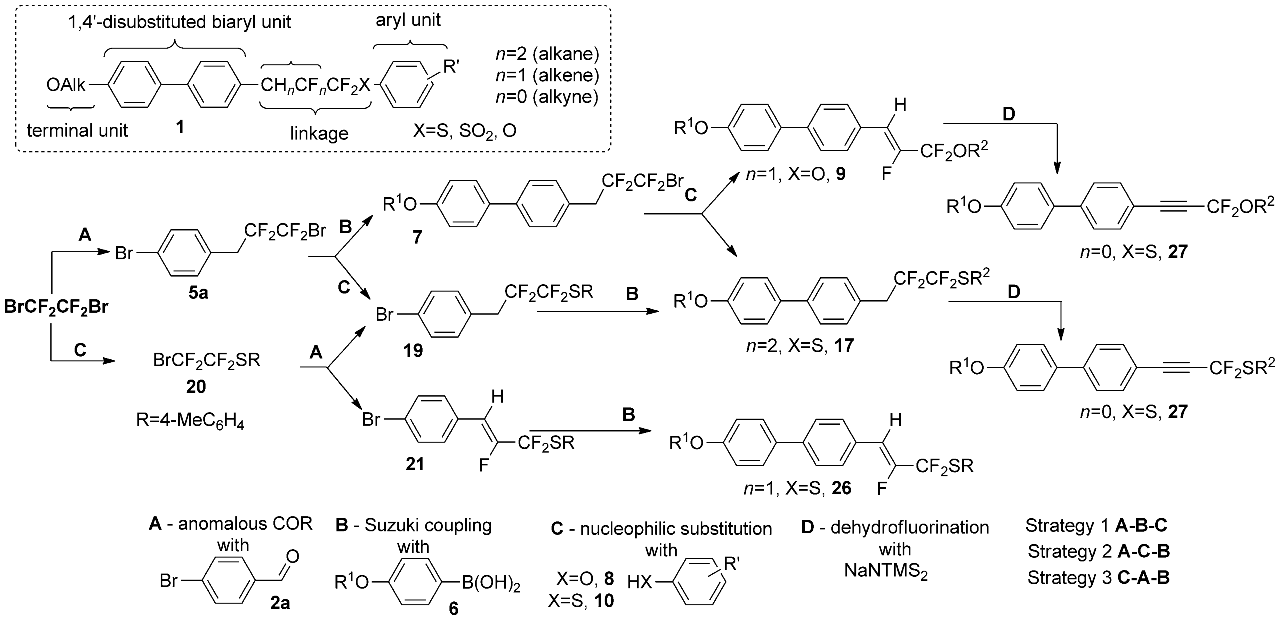
Figure 2. General moiety of the calamitic liquid-crystal.

Having these considerations in mind and 1,2-dibromotetrafluoroethane in hand, we decided to elaborate the synthesis of a new family of compounds **1**, which has all of the structural units mentioned above and, therefore, can reveal liquid-crystalline properties (Scheme 1). The significant feature of our approach is possibility to prepare compounds with variation of all possible fragments of target compounds. Quite important is also possibility to change the nature (electronic and geometrical parameters) of linking fragment Y because our idea was to prepare compounds of alkane ($CH_2CF_2CF_2$ moiety), alkene ($CH{=}CFCF_2$ moiety) and alkyne ($C{\equiv}CCF_2$ moiety) series. Therefore, we expected also a significant variation of LC properties of prepared compounds.

We have developed three effective strategies for assembling the molecular core of compounds **1**. (Scheme 1) All the approaches include three synthetic steps, which are Suzuki coupling (**B**), substitution of bromine in CF_2CF_2Br moiety (**C**) and catalytic olefination reaction (COR) discovered about a decade ago in our group (**A**). COR is a transformation of N-unsubstituted hydrazones **3** of carbonyl compounds **2** into various substituted alkenes **4** by treatment with polyhalogenoalkanes in the presence of catalytic amounts of CuCl.[4] A number of convenient syntheses of various alkenes **4** including fluorinated ones was developed using this reaction.[5] In the case of 1,2-dibromotetrafluoroethane, the catalytic olefination reaction unexpectedly led to anomalous formation of alkanes bearing CF_2CF_2Br fragment instead of the desired alkenes, as a result this reaction opened a new straightforward approach to tetrafluoropropanes derivatives **5**.[5d] (Scheme 2)



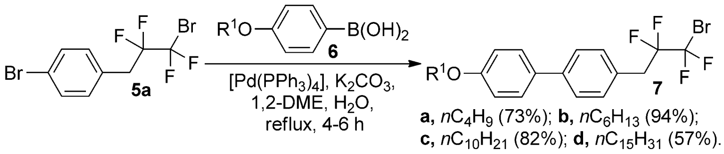
Scheme 2. Catalytic olefination reaction.



Scheme 1. A new family of liquid crystals based on 1,2-dibromotetrafluoroethane and methodology of their synthesis.

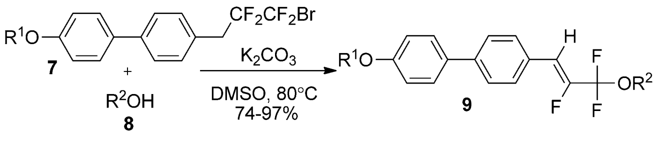
Our first strategy started from the reaction of 1,2-dibromotetrafluoroethane with hydrazone of 4-bromobenzaldehyde **2a** (COR), giving propane **5a** (Scheme 1). Next, Suzuki coupling with arylboronic acids **6** led to the biaryls **7**. The last step is substitution of bromine atom by O- or S nucleophiles **8** or **10**, respectively. In contrast, the last step of strategies 2 and 3 is Suzuki coupling of arylbromides **19** or **21**, obtained by nucleophilic substitution from **5a** (strategy 2) or by COR from **2a** and **20** (strategy 3). Final "tuning" of the desired molecule can be done either by choice of appropriate nucleophile (step **C**, strategy 1, Scheme 1) or the change of type of linkage by using dehydrofluorination (**D**) at the very last step after the core of **1** is assembled. As a result a family of alkanes, alkenes, and acetylenes can be prepared. In addition, oxidation of sulfides to sulfones provides some more compounds in the set.

Synthesis of 1 by using strategy 1: At first step of the sequence propane **5a** was prepared in one pot by anomalous COR using our earlier reported procedure (Scheme 2).[5d] Suzuki coupling of arylbromide **5a** with boronic acids **6** led chemoselectively to a series of biaryls **7** in high yields (Scheme 3). The reaction was carried out in 1,2-dimethoxyethane in the presence of K_2CO_3 and under $Pd(PPh_3)_4$ catalysis.[6] Only the bromine in the benzene ring is replaced with an aryl moiety; the observed chemoselectivity can be explained by higher activity of aryl bromine atom compared with the bromine in the fluorinated alkyl chain. In all cases only **7** was isolated without any traces of the alternative products.



Scheme 3. Synthesis of biaryls **7**.

Next, we investigated nucleophilic substitution of **7** with various phenols **8**. Reactions were carried out in DMSO by using K_2CO_3 as a base. A moderately elevated temperature was needed for complete transformation of starting materials. Under these basic conditions, substitution of bromine with phenolates led also to subsequent dehydrofluorination. As a result, a set of fluorinated alkenes **9a–l** (Scheme 4, Table 1) were prepared in high to almost quantitative yields.



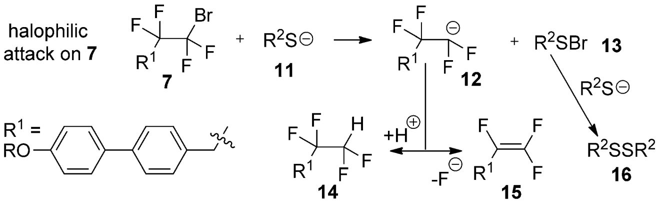
Scheme 4. Nucleophilic substitution in bromides **7** with phenols **8**.

Table 1. Preparation of CF_2O-bridged alkenes **9**.

9	R^1	R^2	Yield of **9** [%]	**9**	R^1	R^2	Yield of **9** [%]
a	*n*-C_6H_{13}	4-MeC_6H_4	85	**g**	*n*-C_6H_{13}	2-(*t*Bu)C_6H_4	76
b	*n*-C_6H_{13}	3-MeC_6H_4	80	**h**	*n*-C_6H_{13}	3,4-$(OMe)_2C_6H_3$	76
c	*n*-C_6H_{13}	2-MeC_6H_4	82	**i**	*n*-C_6H_{13}	4-ClC_6H_4	81
d	*n*-C_6H_{13}	4-(*sec*-Bu)C_6H_4	91	**j**	*n*-C_4H_9	4-(*sec*-Bu)C_6H_4	90
e	*n*-C_6H_{13}	4-(*n*-Oct)C_6H_4	74	**k**	*n*-$C_{10}H_{21}$	4-(*sec*-Bu)C_6H_4	97
f	*n*-C_6H_{13}	2-FC_6H_4	92	**l**	*n*-$C_{15}H_{31}$	4-(*sec*-Bu)C_6H_4	87

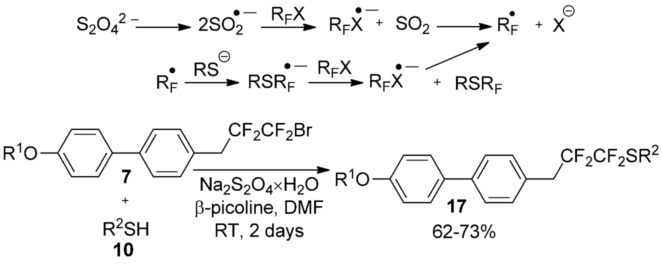
The reaction proceeded 100% stereoselectively to afford pure *Z* isomers of **9**. The configuration of which was determined by ^{1}H NMR spectroscopy. The $^3J_{H-F}$ coupling constants of vicinal vinylic hydrogen and fluorine are in the range of 32–35 Hz, which pointed undoubtedly their *trans*-arrangement at the double bond and the *Z* configuration of this bond.[7]

We also investigated reactions of compounds **7** with thiophenols **10** under similar conditions. To our surprise, the more nucleophilic thiophenols **10** did not give the expected sulfides at all. The reaction proceeded very slowly, accompanied with tarring and dehydrofluorination. It is known that reaction of polyfluorinated halides with nucleophiles can proceed through a number of various mechanisms including so-called halophilic nucleophilic substitution.[8] Accordingly, halophilic attack of thiophenolates **11** on fluorinated bromides **7** leads to intermediate formation of anion **12**, followed by formation of sulfenylbromides **13** (Scheme 5). Protonation or β-elimination of anion **12** affords alkane **14** and alkene **15**, respectively. The reaction of sulfenylbromide **13** with thiophenolate **11** leads to disulfide **16**. As a result no desired sulfides are formed.



Scheme 5. Reaction of fluorinated bromides **7** with thiophenolates **11** through a halophilic attack.

To our delight, we found that the desired transformation can be successfully performed in the presence of sodium dithionite, which is an efficient mediator of radical reactions through the formation of the radical anion $SO_2^{\cdot-}$. The utility of sodium dithionite has been demonstrated previously for the synthesis of various sulfides from thiols by reaction with some perfluorinated compounds.[9] The reaction of bromides **7** with thiols **10** was carried out in very mild conditions in DMF at room temperature by using β-picoline as a base (Scheme 6). The reaction occurs through a radical mechanism to give corresponding sulfides **17** in good yields (Table 2).

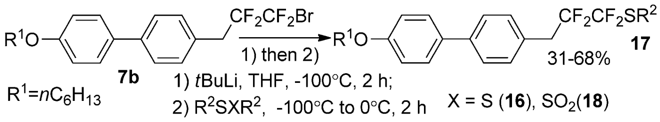


Scheme 6. Transformation of bromides **7** into sulfides **17** in the presence of $Na_2S_2O_4xH_2O$.

Table 2. Preparation of sulfides **17** with CF_2CF_2 bridge.

17	R^1	R^2	Yield of **17** [%]
a	*n*-C_4H_9	4-MeC_6H_4	68
b	*n*-C_6H_{13}	4-MeC_6H_4	65
c	*n*-$C_{10}H_{21}$	4-MeC_6H_4	73
d	*n*-$C_{15}H_{31}$	4-MeC_6H_4	72
e	*n*-C_6H_{13}	Ph	63
f	*n*-C_6H_{13}	4-$MeOC_6H_4$	66

In addition, we used another tactic to perform the desired transformation: umpolung or polarity inversion. It was reported in the literature that perfluoroalkyllithiums are thermally unstable species, which have to be maintained at very low temperatures. For example, a half-life time of C_2F_5Li in ethereal solution is about 8 h at −78 °C,[10] whereas perfluoroheptyl and perfluoropropyl lithium are stable at −90 °C and decompose very rapidly at −75 °C.[11] That is why we performed all the reactions at very low temperature (−100 °C) to minimize the side β-elimination of lithium fluoride. We found that about 2 h was needed for complete bromine–lithium exchange at this temperature, when *t*BuLi was used (*n*-BuLi gave worse results due to a lower rate of bromine–lithium exchange). Subsequent treatment of intermediate alkyllithiums with disulfides led to the corresponding sulfides **17** in moderate to good yields (Scheme 7). The reaction was very slow in case of less electrophilic disulfides **16** such as 2,4,6-trimethylphenyl (mesityl) disulfide and 4-methoxyphenyl disulfide. However, using the corresponding sulfonothioates **18** enables the preparation of the target sulfides quite effectively (Scheme 7 and Table 3). Even the sterically hindered mesityl-substituted target sulfide **17k** was prepared in a reasonably good yield (Table 3). The transformation has a general character, allowing preparation of alkyl- as well as aryl substituted sulfides. Thus, by means of strategy 1 a series of CF_2O bridged alkenes **7** and CF_2CF_2S bridged alkanes **17** were prepared (Table 3).



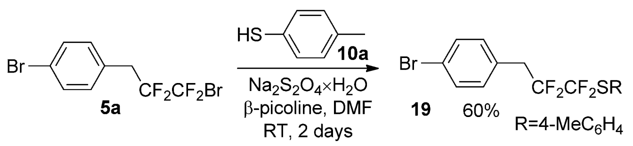
Scheme 7. Transformation of bromide **7b** into sulfides **17**.

Table 3. Preparation of sulfides **17** with CF_2CF_2 bridge.

17	R^2	Yield of **17** [%]
b	4-MeC_6H_4	68
e	Ph	59
f	4-$MeOC_6H_4$	31 (X = SO_2)
g	Me	47
h	*n*-Bu	53
i	2-Naphtyl	63
j	4-(*i*Pr)C_6H_4	52
k	Mesityl	53 (X = SO_2)
l	4-FC_6H_4	46 (X = SO_2)

Synthesis of 1 using strategies 2 and 3: The similarity of strategies 2 and 3 is using Suzuki coupling on the very last step of the synthetic pathway. In fact they are equal by this step. One can also say that in both strategies transformation of both sides of 1,2-dibromoethane is firstly performed followed by final creation of biaryl moiety.

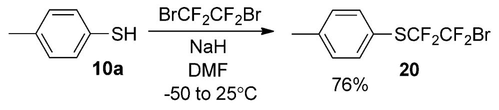
The first step of strategy **2** is the synthesis of propane **5a** by anomalous COR from 4-bromobenzaldehyde **2a**, so it is completely the same this step in strategy **1**. Next, transformation of **5a** occurs by reaction with 4-methylthiophenol **10a** in the presence of sodium dithionite (radical conditions) to give sulfide **19** in 60 % yield (Scheme 8). The reaction again proceeds 100 % chemoselectively involving only substitution at alkylbromide moiety.



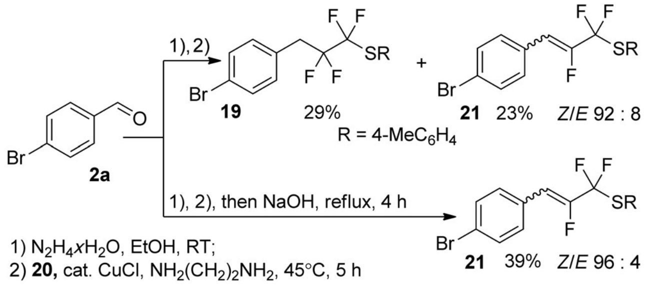
Scheme 8. Nucleophilic substitution of bromine in **5a** with 4-methylthiophenol **10a** in the presence of sodium dithionate.

Substitution of bromine in 1,2-dibromotetrafluoroethane by a nucleophile is the first step of our strategy **3**. The reaction of 1,2-dibromotetrafluoroethane with sodium 4-methylphenylthiolate in DMF led smoothly to sulfide **20** in 76 % yield (Scheme 9).

Next, olefination of 4-bromobenzaldehyde **2a** by bromotetrafluoroethane **20** was investigated. The reaction was performed in one-pot version without isolation of intermediate hydrazone. It was found that the optimal conditions for this reaction are heating in EtOH at 45 °C, using ethylenedi-



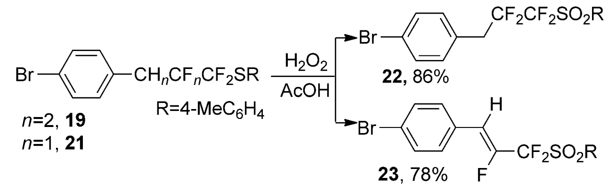
Scheme 9. Nucleophilic substitution of bromine in $BrCF_2CF_2Br$ with 4-methylphenylthiolate.



Scheme 10. COR of 4-bromobenzaldehyde **5a** and sulfide **20**.

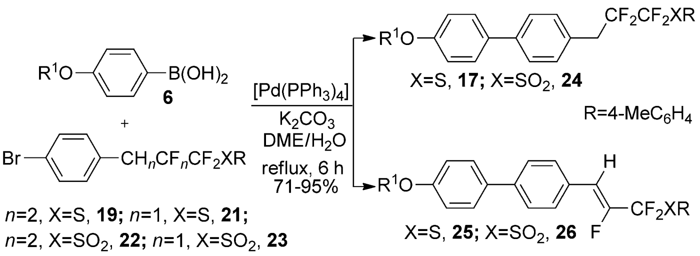
amine as a base. In contrast to 1,2-dibromotetrafluoroethane, the desired alkane **19** was prepared in mixture with alkene **21** (Scheme 10). However, it should be noted, that the mixture of alkane **19** and alkene **21** is easily separated by using column chromatography. Moreover, addition of sodium hydroxide to the reaction mixture followed by heating at reflux for 4 h led exclusively to alkene **21** in 39 % yield (Scheme 10). Formation of alkene **21** is highly stereoselective process, giving mostly the *Z* isomer. Assignment of the isomers was performed by comparing values of the $^3J_{H\text{-}F}$ coupling constants of vicinal vinylic hydrogen and fluorine in ^{1}H NMR spectroscopy. In the case of the *Z* isomer, the corresponding value (35.5 Hz) is higher than for *E* isomer (21.2 Hz).

To expand the synthetic scope of strategies 2 and 3, we carried out oxidation of sulfides **19** and **21** into sulfones by using 40 % H_2O_2 in acetic acid heated to reflux to form sulfones **22** and **23** in high yields (Scheme 11).



Scheme 11. Oxidation of sulfides **19** and **21** into sulfones **22** and **23**.

Suzuki coupling of sulfides **19** or **21** and sulfones **22** or **23** with boronic acids **6** in a mixture of 1,2-DME/water (heated to relux) smoothly gave the corresponding biaryls **17** and **24–26** in high yields (Scheme 12 and Table 4**).**



Scheme 12. Coupling of aryl bromides **19** and **21** and **22** and **23** with boronic acids **6**.

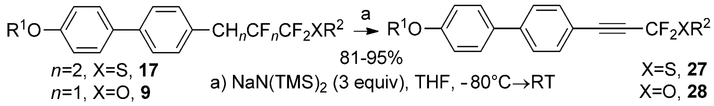
Table 4. Preparation of compounds **17** and **24–26**.

Compound	R^1	Yield [%]	Compound	R^1	Yield [%]
17a	n-C_4H_9	81	**25b**	n-C_6H_{13}	82
17c	n-$C_{10}H_{21}$	82	**25c**	n-$C_{10}H_{21}$	85
17d	n-$C_{15}H_{31}$	80	**25d**	n-$C_{15}H_{31}$	76
17m	n-$C_{18}H_{37}$	74	**25e**	n-$C_{18}H_{37}$	71
24a	n-C_4H_9	91	**26a**	n-C_4H_9	85
24b	n-C_6H_{13}	83	**26b**	n-C_6H_{13}	81
24c	n-$C_{10}H_{21}$	86	**26c**	n-$C_{10}H_{21}$	81
25a	n-C_4H_9	84			

Thus, strategies 2 and 3 were successfully realized, providing an alternative approach to biaryls **1**. Compared with strategy 1, these sequences are less flexible because only sulfides with the 4-tolyl substituent can be obtained. Furthermore, the simplicity of experimental protocol makes these strategies more appropriate for synthesis of these sulfides.

Synthesis of acetylenes 27 and 28: At the final stage we have also prepared CF_2O and CF_2S-substituted alkynes as promising candidates for LC study. Elimination of hydrogen fluoride by using LDA as a base did not lead to desired alkynes, giving mostly a strong tarring. This fact can be explained by nucleophilic addition of diisopropyl amine to form the alkyne, which was found to occur easily in case of fluorinated alkynes.[12] However, the use of less nucleophilic sodium hexamethyldisilazide is allowed for efficient elimination, producing corresponding CF_2S alkynes **27** in high yields. Also, this approach is suitable for dehydrofluorination of alkenes **17**. Alkynes **28** were synthesized in high yields by treatment of vinylfluorides **9** with $NaNTMS_2$ (Scheme 13 and Table 5).

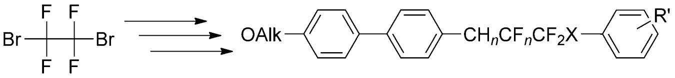
So, on the base of available 1,2-dibromotetrafluoroethane a new approach to a manifold of CF_2CF_2S-, CF_2S- and CF_2O-bridged molecules **1** was elaborated (Scheme 14). Three alternative strategies were proposed providing a ver-



Scheme 13. Preparation of acetylenes **27** and **28**.

Table 5. Preparation of alkynes **27** and **28**.

Alkyne	X	R^1	R^2	Yield [%]
27a	S	n-C_4H_9	4-MeC_6H_4	85
27b	S	n-C_6H_{13}	4-MeC_6H_4	83
27c	S	n-$C_{10}H_{21}$	4-MeC_6H_4	85
27d	S	n-$C_{18}H_{37}$	4-MeC_6H_4	91
28a	O	n-C_6H_{13}	4-MeC_6H_4	93
28b	O	n-C_6H_{13}	3-MeC_6H_4	88
28c	O	n-C_6H_{13}	2-MeC_6H_4	95
28d	O	n-C_6H_{13}	4-(*sec*-Bu)C_6H_4	91
28e	O	n-C_6H_{13}	2-FC_6H_4	81
28f	O	n-C_6H_{13}	2-(*t*Bu)C_6H_4	91



Scheme 14. Synthesis of compounds **1** by using 1,2-dibromotetrafluoroethane.

satile tool for directed synthesis of a wide range of fluorinated compounds.

Investigation of liquid crystalline properties: The phase behavior of all compounds was examined by polarizing optical microscopy (POM) and differential scanning calorimetry (DSC). Mesophase sequences and thermal data are collected in Tables 6 and 7.

Compounds **24** and **26**, containing a sulfonyl group, do not form any mesophases and directly transform into the liquid state. Most probably this fact is explained by distortion of calamitic geometry for the sulfones having an angular structure.

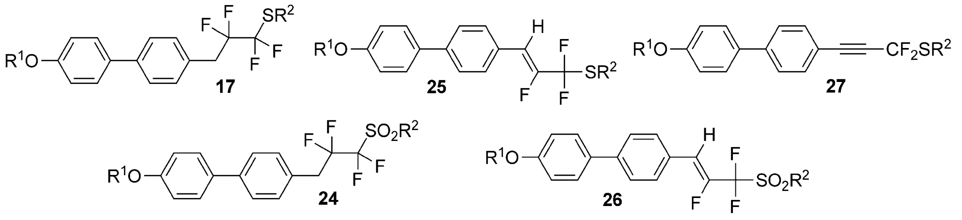


Figure 3. Structures of CF$_2$S(SO$_2$)- and CF$_2$CF$_2$S(SO$_2$)-bridged biphenyls.

Sulfides **17** with an alkane linkage (CH$_2$–CF$_2$–CF$_2$S; Figure 3) have demonstrated only the existence of a nematic LC-phase, although alkenes **25** (CH=CF–CF$_2$S) and alkynes **27** (C≡C–CF$_2$S) have mostly smectic A LC-phase. In all cases, sulfides **17**, **25**, and **27** with C$_4$ side alkyl-chains do not show LC properties. Temperatures of the phase transition into the LC state lie in the range between 67 (**27c**) and 105 °C (**25b**). The range of clearing temperature values is between 87 (**17j**) to 122 °C (**17i**). Among the investigated sulfides, compounds **17l** and **27c** have the widest range of mesophase existence, which are 23 °C and 24 °C, respectively.

Table 6. Phase behaviour and thermal data of sulfides **17**, **25**, and **27**, and sulfones **24** and **26**.

Compound	R^1	Linkage type	Group	R^2	Mesophase sequence [°C] and thermal data [kJ mol^{-1}]
17a	n-C$_4$H$_9$	alkane	S	4-MeC$_6$H$_4$	no mesophases
17b	n-C$_6$H$_{13}$	alkane	S	4-MeC$_6$H$_4$	Cr 95 (21.79) N 104 (1.37) I
17c	n-C$_{10}$H$_{21}$	alkane	S	4-MeC$_6$H$_4$	Cr 83 (16.81) N 104 (3.32) I
17d	n-C$_{15}$H$_{31}$	alkane	S	4-MeC$_6$H$_4$	Cr 85 (30.84) N 94 (3.33) I[a]
17e	n-C$_6$H$_{13}$	alkane	S	Ph	Cr 82 N 90 I
17f	n-C$_6$H$_{13}$	alkane	S	4-MeOC$_6$H$_4$	Cr 82 N 97 I
17g	n-C$_6$H$_{13}$	alkane	S	Me	no mesophases
17h	n-C$_6$H$_{13}$	alkane	S	nBu	no mesophases
17i	n-C$_6$H$_{13}$	alkane	S	2-Naphtyl	Cr 115 N 122 I
17j	n-C$_6$H$_{13}$	alkane	S	4-(iPr)C$_6$H$_4$	Cr 73 N 87 I
17k	n-C$_6$H$_{13}$	alkane	S	Mesityl	no mesophases
17l	n-C$_6$H$_{13}$	alkane	S	4-FC$_6$H$_4$	Cr 70 N 93 I
17m	n-C$_{18}$H$_{37}$	alkane	S	4-MeC$_6$H$_4$	no mesophases
25a	n-C$_4$H$_9$	alkene	S	4-MeC$_6$H$_4$	no mesophases
25b	n-C$_6$H$_{13}$	alkene	S	4-MeC$_6$H$_4$	Cr 105 (24.31) N 112 (1.64) I
25c	n-C$_{10}$H$_{21}$	alkene	S	4-MeC$_6$H$_4$	Cr 95 (28.18) S$_B$ 102 S$_A$ 110 (4.42) I[b]
25d	n-C$_{15}$H$_{31}$	alkene	S	4-MeC$_6$H$_4$	no mesophases
25e	n-C$_{18}$H$_{37}$	alkene	S	4-MeC$_6$H$_4$	Cr 85 (41.77) S$_A$ 104 (6.54) I
27a	n-C$_4$H$_9$	alkyne	S	4-MeC$_6$H$_4$	no mesophases
27b	n-C$_6$H$_{13}$	alkyne	S	4-MeC$_6$H$_4$	no mesophases
27c	n-C$_{10}$H$_{21}$	alkyne	S	4-MeC$_6$H$_4$	Cr 67 (33.31) S$_A$ 91 (12.03) I
27d	n-C$_{18}$H$_{37}$	alkyne	S	4-MeC$_6$H$_4$	Cr 76 (52.22) S$_A$ 95 (7.73) I
24	[c]	alkanes	SO$_2$	4-MeC$_6$H$_4$	no mesophases
26	[c]	alkenes	SO$_2$	4-MeC$_6$H$_4$	no mesophases

[a] After cooling another phase (S$_A$) was found at 76 °C (4.42 kJ mol^{-1}); [b] Corresponding transition values of S$_A$ and S$_B$ were not resolved; [c] R^1 = (**a**) n-C$_4$H$_9$, (**b**) n-C$_6$H$_{13}$, (**c**) n-C$_{10}$H$_{21}$.

CF$_2$O-Bridged compounds revealed better LC properties. Both alkenes **9** and alkynes **28** form mesophases. Smectic, nematic or both phases simultaneously were detected for compounds **9** and **28** (Figure 4). Compound **9i** has the sequence of smectic A, smectic C and nematic mesophases.

The widest ranges of mesophase existence were observed in case of compounds p-Me **9a** and p-Cl **9i** substituents. The corresponding values are 60 and 62 °C, repectively.

This preliminary study of liquid crystalline properties for the set of compounds synthesized shows that the mesophase can exist for almost any substituent. The new type of fluorinated liquid crystals seem amenable to futher study and tuning of desirable physical properties. The effective preparation of O- and S-substituted LC candidates from the same starting building blocks opens the possibility for broad screening in this field. It should be noted the possibility of variation of any part of target molecules including the nature of bond connecting the key fragments resulting in diversity of new liquid crystals.

Conclusion

A simple and straightforward three-step synthesis of new family of fluorinated liquid crystals was elaborated. The catalytic olefination reaction was used as a key step in the synthetic sequences. Vari-

Table 7. Phase behavior and thermal data of CF_2O alkenes **9** and alkynes **28**.

Compound	R^1	Linkage type	R^2	Mesophase sequence [°C] and thermal data [kJ mol^{-1}]
9a	n-C_6H_{13}	alkene	4-MeC_6H_4	Cr 78 (15.74) S_A 103 (2.47) (2.78) N 138 (1.62) I
9b	n-C_6H_{13}	alkene	3-MeC_6H_4	Cr 78 S_A 106 I
9c	n-C_6H_{13}	alkene	2-MeC_6H_4	Cr 67 (14.51) S_A 86 (3.59) N 90 (2.47) I
9d	n-C_6H_{13}	alkene	4-(*sec*-Bu)C_6H_4	Cr 78 (12.78) S_C 94 (1.67) N 109 (1.07) I
9e	n-C_6H_{13}	alkene	4-(n-Oct)C_6H_4	Cr 65 S_A 85 I
9f	n-C_6H_{13}	alkene	2-FC_6H_4	Cr 70 S_A 101 I
9g	n-C_6H_{13}	alkene	2-(tBu)C_6H_4	no mesophases
9h	n-C_6H_{13}	alkene	3,4-$(OMe)_2C_6H_4$	no mesophases
9i	n-C_6H_{13}	alkene	4-ClC_6H_4	Cr 94 (25.02) S_A 122 (3.33) S_C 135 (1.14) N 156 I
9j	n-C_4H_9	alkene	4-(*sec*-Bu)C_6H_4	Cr 91 N 113 I
9k	n-$C_{10}H_{21}$	alkene	4-(*sec*-Bu)C_6H_4	Cr 71 S_A 84 N 95 I
9l	n-$C_{15}H_{31}$	alkene	4-(*sec*-Bu)C_6H_4	Cr 103 S_A 119 I
28a	n-C_6H_{13}	alkyne	4-MeC_6H_4	Cr 68 S_A 80 I
28b	n-C_6H_{13}	alkyne	3-MeC_6H_4	no mesophases
28c	n-C_6H_{13}	alkyne	2-MeC_6H_4	no mesophases
28d	n-C_6H_{13}	alkyne	4-(*sec*-Bu)C_6H_4	Cr 46 S_A 64 I
28e	n-C_6H_{13}	alkyne	2-FC_6H_4	no mesophases
28f	n-C_6H_{13}	alkyne	2-(tBu)C_6H_4	no mesophases

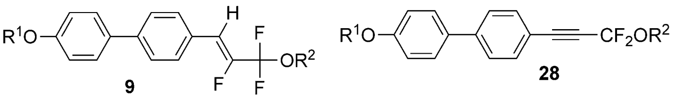


Figure 4. Structures of CF_2O-bridged biphenyls.

ous fluorinated CF_2CF_2S-bridged alkanes and CF_2S-, CF_2O-bridged alkenes and alkynes can be obtained by this method. A significant number of the prepared compounds demonstrated attractive LC properties. CF_2O-bridged alkenes revealed widest range of mesophase existence among prepared compounds. Simplicity of reaction procedures, high universality, and perspective liquid-crystalline properties of the obtained compounds may provide broad opportunities in the design and synthesis of new liquid crystals by using the elaborated method.

Experimental Section

General: All reactions were monitored by thin-layer chromatography carried out on Merck silica gel plates (Silufol UV-254). Column chromatography was performed on silica gel (Merck, 63–200 mesh). ^1H NMR and ^{13}C NMR spectra were recorded on Bruker AMX 400 at 400 and 100 MHz respectively. ^{19}F NMR spectra were recorded on a Bruker AMX Avance 400 (377 MHz), Bruker ARX 300 (287 MHz) or Bruker DXP 200 (188 MHz). Compounds were dissolved in $CDCl_3$ and [D$_6$]acetone. Tetramethylsilane and CCl_3F were used as internal standards. Mesophase sequences were measured by polarizing microscopy on POLAM P-211 and DSC on hot stage Mettler FP82 (Central processor Mettler FP80). IR spectra were recorded on ThermoNicolet IR 200. Mass spectra (HRMS (ESI)) were measured on a Bruker micrOTOF II and MicroTof Bruker Daltonics. Compound **5a** were prepared by the method reported previously.[5d] Synthesis of boronic acids **6** was carried out in 2 steps using a modification of previously described synthetic protocols. Firstly, 4-bromophenol was alkylated by long chain alkylbromides.[13] After that, thus obtained arylbromides were converted into boronic acids **6** by treatment with n-BuLi followed by reaction with trimethylborate.[14]

Synthesis of the CF_2O-alkenes 9 by nucleophilic substitution of bromine with phenolates (general procedure): The corresponding bromide **7** (0.5 mmol), phenol **8** (1.0 mmol), K_2CO_3 (345 mg, 2.5 mmol) and DMSO (15 mL) were mixed in a Shlenk tube, then purged with argon and maintained for 6–48 h at 80 °C (TLC control). The reaction mixture was quenched with water (100 mL), the aqueous phase was extracted with CH_2Cl_2 (3×60 mL), the combined organic layers were washed with brine (3×50 mL), water (2×50 mL), and dried over $CaCl_2$. The solvents were evaporated, the residue was purified by chromatography on silica gel (eluent: hexane/CH_2Cl_2 = 4:1; **9h**: hexane/CH_2Cl_2 = 2:1)

(*Z*)-4-(Hexyloxy)-4′-(2,3,3-trifluoro-3-(*p*-tolyloxy)prop-1-enyl)-biphenyl (9a): White solid, yield 85%; R_f = 0.4 (hexane/CH_2Cl_2 = 4:1); ^1H NMR (400 MHz, $CDCl_3$): $\delta = 0.97$ (t, $J = 6.7$ Hz, 3H; CH_3), 1.37–1.45 (m, 4H; CH_2), 1.53 (quin, $J = 7.2$ Hz, 2H; CH_2), 1.85 (quin, $J = 7.1$ Hz, 2H; CH_2), 2.39 (s, 3H; CH_3), 4.04 (t, $J = 6.4$ Hz, 2H; CH_2O), 6.47 (d, $J_{HF} = 36.4$ Hz, 1H; CH=CF), 7.02 (d, $J = 8.6$ Hz, 2H; Ar), 7.18–7.23 (m, 4H; Ar), 7.56–7.68 ppm (m, 6H; Ar); ^{19}F NMR (188 MHz, $CDCl_3$): $\delta = -74.2$ (d, $J = 13.0$ Hz; CF_2-O), −129.5 ppm (dt, $J_{H\text{-}F} = 36.4$ Hz, $J = 13.0$ Hz; CF=CH); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 14.0$, 20.8, 22.6, 25.7, 29.2, 31.6, 68.1 (CH$_2$O), 110.1 (d, $J_{CF} = 2.9$ Hz), 114.9, 117.5 (td, $^1J_{CF} = 277.2$ Hz, $^2J_{CF} = 37.3$ Hz; CF$_2$-CF,), 121.8, 126.7, 128.0, 128.7, 128.9 (d, $J_{CF} = 2.9$ Hz), 130.0, 132.4, 135.9, 141.3, 147.5, 147.7 (dt, $^1J_{CF} = 267.1$ Hz, $^2J_{CF} = 37.3$ Hz, CF-CF_2), 159.1 ppm; IR (neat): $\tilde{\nu} = 1480$, 1610 (Ar), 1700 cm^{-1} (C=C); HRMS (ESI): m/z calcd for $C_{28}H_{29}F_3NaO_2^+$: 477.2012 [M+Na$^+$]; found: 477.2008;

(*Z*)-4-(Hexyloxy)-4′-(2,3,3-trifluoro-3-(*m*-tolyloxy)prop-1-enyl)biphenyl (9b): White solid, yield 80%; R_f = 0.4 (hexane/CH_2Cl_2 = 4:1); ^1H NMR (400 MHz, $CDCl_3$): $\delta = 0.96$ (t, $J = 6.6$ Hz, 3H; CH_3), 1.36–1.43 (m, 4H; CH_2), 1.51 (quin, $J = 7.1$ Hz, 2H; CH_2), 1.84 (quin, $J = 7.1$ Hz, 2H; CH_2), 2.41 (s, 3H; CH_3), 4.04 (t, $J = 6.6$ Hz, 2H; CH_2O), 6.47 (d, $J_{HF} = 36.4$ Hz, 1H; CH=CF), 7.01 (d, $J = 8.6$ Hz, 2H; Ar), 7.09–7.14 (m, 3H; Ar), 7.29 (t, $J = 8.1$ Hz, 1H; Ar), 7.55–7.68 ppm (m, 6H; Ar); ^{19}F NMR (188 MHz, $CDCl_3$): $\delta = -74.1$ (d, $J = 13.0$ Hz; CF_2-O), −129.5 ppm (dt, $J_{H\text{-}F} = 36.4$ Hz, $J = 13.0$ Hz; CF=CH); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 14.0$, 21.2, 22.6, 25.7, 29.2, 31.6, 68.0 (CH$_2$O), 110.1 (d, $J_{CF} = 2.9$ Hz), 117.5 (td, $^1J_{CF} = 261.3$ Hz, $^2J_{CF} = 38.1$ Hz; CF$_2$-CF,), 118.8, 122.5, 126.7, 126.9, 127.9, 128.7, 128.8 (d, $^4J_{CF} = 3.7$ Hz), 129.2, 130.0 (d, $^4J_{CF} = 7.3$ Hz), 132.3, 139.7, 141.3, 147.7 (dt, $^1J_{CF} = 267.9$ Hz, $^2J_{CF} = 38.1$ Hz; CF-CF$_2$,), 149.7, 159.1 ppm; IR (neat): $\tilde{\nu} = 1480$, 1610 (Ar), 1680 cm^{-1} (C=C); HRMS (ESI): m/z calcd for $C_{28}H_{29}F_3NaO_2^+$: 477.2017 [M+Na$^+$]; found: 477.2021.

(*Z*)-4-(Hexyloxy)-4′-(2,3,3-trifluoro-3-(*o*-tolyloxy)prop-1-enyl)biphenyl (9c): White solid, yield 82%; R_f = 0.4 (hexane/CH_2Cl_2 = 4:1); IR (neat): ^1H NMR (400 MHz, $CDCl_3$): $\delta = 0.97$ (t, $J = 6.7$ Hz, 3H; CH_3), 1.37–1.44 (m, 4H; CH_2), 1.53 (quin, $J = 7.5$ Hz, 2H; CH_2), 1.85 (quin, $J = 7.1$ Hz, 2H; CH_2), 2.39 (s, 3H; CH_3), 4.04 (t, $J = 6.6$ Hz, 2H; CH_2O), 6.52 (d, $J_{HF} = 36.4$ Hz, 1H; CH=CF), 7.02 (d, $J = 8.8$ Hz, 2H; Ar), 7.18–7.35 (m, 4H; Ar), 7.56–7.70 ppm (m, 6H; Ar); ^{19}F NMR (188 MHz, $CDCl_3$): $\delta = -74.9$ (d, $J = 13.0$ Hz; CF_2-O), −130.1 ppm (dt, $J_{HF} = 36.4$ Hz, $J = 13.0$ Hz; CF=CH); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 14.0$, 16.4, 22.6, 25.7, 29.2, 31.6, 68.0 (CH$_2$O), 110.0 (d, $J_{CF} = 2.9$ Hz), 114.8, 117.6 (td, $^1J_{CF} = 260.5$ Hz, $^2J_{CF} = 37.3$ Hz; CF$_2$-CF,), 122.1, 126.1, 126.7, 128.0, 128.7, 128.8 (d, $^4J_{CF} = 2.9$ Hz), 130.0 (d, $^4J_{CF} = 7.3$ Hz), 131.3, 131.4, 132.4, 141.3, 147.8 (dt, $^1J_{CF} = 267.9$ Hz, $^2J_{CF} = 37.7$ Hz; CF-CF$_2$,), 148.2, 159.1 ppm; $\tilde{\nu} = 1480$, 1610 (Ar), 1700 cm^{-1} (C=C); HRMS (ESI): m/z calcd for $C_{28}H_{29}F_3NaO_2^+$: 477.1949 [M+Na$^+$]; found: 477.1986.

(*Z*)-4-(3-(4-*sec*-Butylphenoxy)-2,3,3-trifluoroprop-1-enyl)-4′-(hexyloxy)biphenyl (9d): white solid, yield 91%; R_f = 0.4 (hexane/CH_2Cl_2 = 4:1); ^1H NMR (400 MHz, $CDCl_3$): $\delta = 0.86$ (t, $J = 7.3$ Hz, 3H; CH_3), 0.96 (t, $J = 6.7$ Hz, 3H; CH$_3$,), 1.27 (d, $J = 6.8$ Hz, 3H; CH_3), 1.37–1.44 (m, 4H;

CH_2), 1.52 (quin, $J=7.3$ Hz, 2H; CH_2), 1.62 (quin, $J=7.3$ Hz, 2H; CH_2), 1.84 (quin, $J=7.1$ Hz, 2H; CH_2), 2.64 (sex, $J=7.0$ Hz, 1H; $\mathit{CH}CH_3$), 4.04 (t, $J=6.6$ Hz, 2H; CH_2O), 6.47 (d, $J_{HF}=36.4$ Hz, 1H; CH=CF), 7.01 (d, $J=8.6$ Hz, 2H; Ar), 7.20–7.23 (m, 4H; Ar), 7.54–7.68 ppm (m, 6H; Ar); ^{19}F NMR (188 MHz, $CDCl_3$): $\delta=-74.2$ (d, $J=13.0$ Hz; CF_2-O), -129.5 ppm (dt, $J_{HF}=36.4$ Hz, $J=13.0$ Hz; CF=CH); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=12.1$, 14.0, 21.7, 22.6, 25.7, 29.3, 31.2, 31.6, 41.1, 68.0 (CH_2O), 110.1, 114.8, 117.5 (td, $^1J_{CF}=259.8$ Hz, $^2J_{CF}=37.3$ Hz; CF_2-CF,), 121.7, 126.7, 127.9, 128.7, 128.8 (d, $^4J_{CF}=3.7$ Hz), 130.0 (d, $^4J_{CF}=7.3$ Hz), 132.3, 141.3, 145.6, 147.6, 147.8 (dt, $^1J_{CF}=267.9$ Hz, $^2J_{CF}=38.1$ Hz; CF-CF_2), 159.1 ppm; IR (neat): $\tilde{\nu}=1480$, 1610 (Ar), 1700 cm^{-1} (C=C); HRMS (ESI): m/z calcd for $C_{31}H_{35}F_3NaO_2^+$: 519.2481 $[M+Na^+]$; found: 519.2467;

(Z)-4-(Hexyloxy)-4′-(2,3,3-trifluoro-3-(4-octylphenoxy)prop-1-enyl)biphenyl (9e): White solid, yield 74%; $R_f=0.4$ (hexane/$CH_2Cl_2=4:1$); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=0.78$ (t, $J=6.1$ Hz, 3H; CH_3), 0.98 (t, $J=7.1$ Hz, 3H; CH_3), 1.37–1.45 (m, 18H; CH_2), 1.53 (quin, $J=7.3$ Hz, 2H; CH_2), 1.86 (quin, $J=7.0$ Hz, 2H; CH_2), 4.05 (t, $J=6.6$ Hz, 2H; CH_2O), 6.47 (d, $J_{HF}=36.4$ Hz, 1H; CH=CF), 7.03 (d, $J=8.6$ Hz, 2H; Ar), 7.22 (d, $J=8.6$ Hz, 2H; Ar), 7.42 (d, $J=8.6$ Hz, 2H; Ar), 7.56–7.68 ppm (m, 6H; Ar); ^{19}F NMR (188 MHz, $CDCl_3$): $\delta=-74.3$ (d, $J=13.0$ Hz; CF_2-O), -129.4 ppm (dt, $J_{HF}=36.4$ Hz, $J=13.0$ Hz; CF=CH); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=14.0$, 22.6, 25.7, 29.3, 31.5, 31.6–31.7 (m, 5CH_2), 32.3, 38.3, 57.0, 68.0 (CH_2O), 110.1 (d, $J_{CF}=2.2$ Hz), 114.9, 117.5 (td, $^1J_{CF}=259.8$ Hz, $^2J_{CF}=37.3$ Hz; CF_2-CF,), 121.1, 126.7, 127.2, 128.0, 128.7, 128.8 (d, $J_{CF}=3.7$ Hz), 130.0 (d, $J_{CF}=7.3$ Hz), 132.4, 141.3, 147.7 (dt, $^1J_{CF}=267.9$ Hz, $^2J_{CF}=37.3$ Hz; CF-CF_2), 148.0, 159.1 ppm; IR (neat): $\tilde{\nu}=1480$, 1600 (Ar), 1680 cm^{-1} (C=C); HRMS (ESI): m/z calcd for $C_{35}H_{43}F_3NaO_2^+$:575.3107 $[M+Na^+]$; found: 575.3111.

(Z)-4-(Hexyloxy)-4′-(2,3,3-trifluoro-3-(2-fluorophenoxy)prop-1-enyl)biphenyl (9f): White solid, yield 92%; $R_f=0.4$ (hexane/$CH_2Cl_2=4:1$); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=0.95$ (t, $J=6.8$ Hz, 3H; CH_3), 1.36–1.43 (m, 4H; CH_2), 1.51 (quin, $J=7.1$ Hz, 2H; CH_2), 1.84 (quin, $J=7.0$ Hz, 2H; CH_2), 4.03 (t, $J=6.4$ Hz, 2H; CH_2O), 6.52 (d, $J_{HF}=36.4$ Hz, 1H; CH=CF), 7.00 (d, $J=8.6$ Hz, 2H; Ar), 7.15–7.27 (m, 3H; Ar), 7.41 (t, 1H; Ar), 7.56–7.69 ppm (m, 6H; Ar); ^{19}F NMR (188 MHz, $CDCl_3$): $\delta=-74.8$ (d, $J=13.0$ Hz; CF_2-O), -129.4 (m; Ar-F), -130.0 ppm (dt, $J_{HF}=36.4$ Hz, $J=13.0$ Hz; CF=CH); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=14.0$, 22.6, 25.7, 29.2, 31.6, 68.1 (CH_2O), 110.5 (d, $J_{CF}=2.9$ Hz), 114.9, 117.0 (d, $J_{CF}=19.0$ Hz), 117.5 (td, $^1J_{CF}=262.3$ Hz, $^2J_{CF}=38.8$ Hzl; CF_2-CF,), 124.3 (d, $J_{CF}=4.4$ Hz), 124.8, 126.8, 127.5 (d, $J_{CF}=6.7$ Hz), 128.0, 128.7 (d, $J_{CF}=2.9$ Hz), 130.1 (d, $J_{CF}=7.3$ Hz), 132.4, 136.9, 139.2, 141.5, 147.1 (dt, $^1J_{CF}=267.9$ Hz, $^2J_{CF}=37.3$ Hz; CF-CF_2), 159.1 ppm; IR (neat): $\tilde{\nu}=1500$, 1610 (Ar), 1700 cm^{-1} (C=C); HRMS (ESI): m/z calcd for $C_{27}H_{26}F_4NaO_2^+$: 481.1761 $[M+Na^+]$; found: 481.1745.

(Z)-4-(3-(2-*tert*-Butylphenoxy)-2,3,3-trifluoroprop-1-enyl)-4′-(hexyloxy)biphenyl (9g): White solid, yield 76%; $R_f=0.4$ (hexane/$CH_2Cl_2=4:1$); m.p. 63.4–64.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=0.99$ (t, $J=7.0$ Hz, 3H; CH_3), 1.39–1.45 (m, 4H; CH_2), 1.50 (s, 9H; *t*Bu), 1.55 (quin, $J=7.0$ Hz, 2H; CH_2), 1.87 (quin, $J=7.0$ Hz, 2H; CH_2), 4.06 (t, $J=6.6$ Hz, 2H; CH_2O), 6.56 (d, $J_{HF}=36.4$ Hz, 1H; CH=CF), 7.04 (d, $J=8.2$ Hz, 2H; Ar,), 7.22 (t, 1H; Ar), 7.27 (t, 1H; Ar), 7.45–7.53 (m, 2H; Ar), 7.56–7.72 ppm (m, 6H; Ar); ^{19}F NMR (188 MHz, $CDCl_3$): $\delta=-71.8$ (d, $J=13.0$ Hz; CF_2-O), -128.9 ppm (dt, $J_{H\text{-}F}=36.4$ Hz, $J=13.0$ Hz; CF=CH); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=14.0$, 22.6, 25.7, 29.3, 29.7, 30.2, 31.6, 68.1 (CH_2O), 110.3 (d, $J_{CF}=2.9$ Hz), 114.9, 117.8 (td, $^1J_{CF}=262.0$ Hz, $^2J_{CF}=38.1$ Hz; CF_2-CF,), 119.9, 125.0, 126.8, 127.1, 127.6, 128.0, 128.8 (d, $J_{CF}=3.7$ Hz), 130.0 (d, $^4J_{CF}=7.3$ Hz), 132.38, 140.53, 141.46, 147.98 (dt, $^1J_{CF}=268.6$ Hz, $^2J_{CF}=38.8$ Hz; CF-CF_2), 149.4, 159.1 ppm; IR (neat): $\tilde{\nu}=1480$, 1600 (Ar), 1700 cm^{-1} (C=C); HRMS (ESI): m/z calcd for $C_{31}H_{35}F_3NaO_2^+$: 519.2481 $[M+Na^+]$; found: 519.2487.

(Z)-4-(3-(3,4-Dimethoxyphenoxy)-2,3,3-trifluoroprop-1-enyl)-4′-(hexyloxy)biphenyl (9h): White solid, yield 76%; $R_f=0.4$ (hexane/$CH_2Cl_2=2:1$); m.p. 116.4–118.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=0.94$ (t, $J=7.1$ Hz, 3H; CH_3), 1.35–1.42 (m, 4H; CH_2), 1.51 (quin, $J=7.3$ Hz, 2H; CH_2), 1.84 (quin, $J=6.9$ Hz, 2H; CH_2), 3.91 (s, 3H; CH_3-O), 3.92 (s, 3H; CH_3-O), 4.03 (t, $J=6.6$ Hz, 2H; CH_2O), 6.44 (d, $J_{HF}=36.4$ Hz, 1H; CH=CF), 6.82–6.87 (m, 3H; Ar), 7.00 (d, $J=8.6$ Hz, 2H; Ar), 7.55–7.67 ppm (m, 6H; Ar); ^{19}F NMR (188 MHz, $CDCl_3$): $\delta=-74.6$ (d, $J=13.8$ Hz; CF_2-O), -129.4 ppm (dt, $J_{H\text{-}F}=36.4$ Hz, $J=12.1$ Hz; CF=CH); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=14.0$, 22.6, 25.7, 29.2, 31.6, 55.9 (s; CH_3-O), 56.0 (s; CH_3-O), 68.0 (CH_2O), 106.5, 110.1 (d, $J_{CF}=2.9$ Hz), 111.0, 114.8, 117.5 (td, $^1J_{CF}=265.2$ Hz, $^2J_{CF}=36.6$ Hz; CF_2-CF), 126.7, 127.9, 128.7 (d, $J_{CF}=2.9$ Hz), 129.9 (d, $J_{CF}=7.3$ Hz), 132.3, 139.1, 143.1, 141.3, 147.3, 147.6 (dt, $^1J_{CF}=267.9$ Hz, $^2J_{CF}=35.1$ Hz; CF-CF_2,), 149.3, 159.1 ppm; IR (neat): $\tilde{\nu}=1500$, 1600 (Ar), 1700 cm^{-1} (C=C); HRMS (ESI): m/z calcd for $C_{29}H_{31}F_3NaO_4^+$ $[M+Na^+]$: 523.2067; found: 523.2071.

(Z)-4-(3-(4-Chlorophenoxy)-2,3,3-trifluoroprop-1-enyl)-4′-(hexyloxy)biphenyl (9i): White solid, yield 81%; $R_f=0.4$ (hexane/$CH_2Cl_2=4:1$); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=0.97$ (t, $J=6.7$ Hz, 3H; CH_3), 1.37–1.45 (m, 4H; CH_2), 1.53 (quin, $J=7.2$ Hz, 2H; CH_2), 1.85 (quin, $J=7.0$ Hz, 2H; CH_2), 4.04 (t, $J=6.6$ Hz, 2H; CH_2O), 6.47 (d, $J_{HF}=36.2$ Hz, 1H; CH=CF), 7.02 (d, $J=8.8$ Hz, 2H; Ar), 7.25 (d, $J=8.6$ Hz, 2H; Ar), 7.39 (d, $J=8.8$ Hz, 2H; Ar), 7.54–7.67 ppm (m, 6H; Ar); ^{19}F NMR (188 MHz, $CDCl_3$): $\delta=-74.6$ (d, $J=13.8$ Hz; CF_2-O), -129.9 ppm (dt, $J_{HF}=36.2$ Hz, $J=12.1$ Hz; CF=CH); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=14.0$, 22.6, 25.7, 29.2, 31.6, 68.1 (CH_2O), 110.4 (d, $J_{CF}=2.9$ Hz), 114.9, 117.4 (td, $^1J_{CF}=261.3$ Hz, $^2J_{CF}=38.1$ Hz; CF_2-CF,), 123.3, 126.8, 128.0, 128.6 (d, $J_{CF}=3.6$ Hz), 129.6, 130.0 (d, $J_{CF}=7.3$ Hz), 131.7, 132.3, 141.5, 147.2 (dt, $^1J_{CF}=267.9$ Hz, $^2J_{CF}=38.1$ Hz; CF-CF_2,), 148.2, 159.1 ppm; IR (neat): $\tilde{\nu}=1500$, 1600 (Ar), 1700 cm^{-1} (C=C); HRMS (ESI): m/z calcd for $C_{27}H_{26}ClF_3O_2^+$: 497.1466 $[M+Na^+]$; found: 497.1464.

(Z)-4-Butoxy-4′-(3-(4-*sec*-butylphenoxy)-2,3,3-trifluoroprop-1-enyl)biphenyl (9j): White solid, yield 90%; $R_f=0.4$ (hexane/$CH_2Cl_2=4:1$); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=0.85$ (t, $J=7.5$ Hz, 3H; CH_3), 1.02 (t, $J=7.3$ Hz, 3H; CH_3), 1.26 (d, $J=6.8$ Hz, 3H; CH_3), 1.54 (quin, $J=7.3$ Hz, 2H; CH_2), 1.61 (quin, $J=7.3$ Hz, 2H; CH_2), 1.83 (quin, $J=7.0$ Hz, 2H; CH_2), 2.64 (sex, $J=7.0$ Hz, 1H; $C\mathit{H}CH_3$),4.04 (t, $J=6.6$ Hz, 2H; CH_2O), 6.46 (d, $J_{HF}=36.4$ Hz, 1H; CH=CF), 7.01 (d, $J=8.8$ Hz, 2H; Ar), 7.18–7.23 (m, 4H; Ar), 7.54–7.67 ppm (m, 6H; Ar); ^{19}F NMR (188 MHz, $CDCl_3$): $\delta=-74.3$ (d, $J=13.8$ Hz; CF_2-O), -129.5 ppm (dt, $J_{H\text{-}F}=36.4$ Hz, $J=13.8$ Hz; CF=CH); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=12.1$, 13.8, 19.2, 21.7, 29.7, 31.3, 41.1, 67.7 (CH_2O), 110.1 (d, $J_{CF}=2.9$ Hz), 114.8, 117.5 (td, $^1J_{CF}=259.8$ Hz, $^2J_{CF}=38.1$ Hz; CF_2-CF,), 121.7, 126.7, 128.0, 128.7, 128.9 (d, $^4J_{CF}=2.9$ Hz), 130.0 (d, $^4J_{CF}=6.6$ Hz), 132.4, 141.3, 145.6, 147.6, 147.8 (dt, $^1J_{CF}=268.6$ Hz, $^2J_{CF}=37.3$ Hz; CF-CF_2,), 159.1 ppm; IR (neat): $\tilde{\nu}=1500$, 1610 (Ar), 1700 cm^{-1} (C=C); HRMS (ESI): m/z calcd for $C_{29}H_{31}F_3NaO_2^+$: 491.2168 $[M+Na^+]$; found: 491.2170.

(Z)-4-(3-(4-*sec*-Butylphenoxy)-2,3,3-trifluoroprop-1-enyl)-4′-(decyloxy)biphenyl (9k): White solid, yield 97%; $R_f=0.4$ (hexane/$CH_2Cl_2=4:1$); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=0.95$ (t, $J=7.3$ Hz, 3H; CH_3), 1.04 (t, $J=7.1$ Hz, 3H; CH_3), 1.35 (d, $J=7.1$ Hz, 3H; CH_3), 1.37–1.45 (m, 12H; CH_2), 1.51 (quin, $J=7.1$ Hz, 2H; CH_2), 1.61 (quin, $J=7.3$ Hz, 2H; CH_2), 1.85 (quin, $J=6.9$ Hz, 2H; CH_2), 2.65 (sex, $J=6.9$ Hz, 1H; $C\mathit{H}CH_3$), 4.08 (t, $J=6.4$ Hz, 2H; CH_2O), 6.56 (d, $J_{HF}=36.4$ Hz, 1H; CH=CF), 7.08 (d, $J=8.8$ Hz, 2H; Ar), 7.26–7.34 (m, 4H; Ar), 7.62–7.75 ppm (m, 6H; Ar); ^{19}F NMR (188 MHz, $CDCl_3$): $\delta=-74.2$ (d, $J=13.8$ Hz; CF_2-O), -129.5 ppm (dt, $J_{HF}=36.4$ Hz, $J=13.8$ Hz; CF=CH); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=12.1$, 14.1, 21.7, 22.7, 26.1, 29.3, 29.4, 29.5, 29.6, 29.8, 31.2, 31.9, 41.1, 68.0 (CH_2O), 110.0 (d, $J_{CF}=2.2$ Hz), 114.8, 117.5 (td, $^1J_{CF}=259.8$ Hz, $^2J_{CF}=38.1$ Hz; CF_2-CF,), 121.7, 126.7, 127.9, 128.7, 128.9 (d, $^4J_{CF}=2.9$ Hz), 130.0 (d, $^4J_{CF}=7.3$ Hz), 132.4, 141.3, 145.5, 147.7, 147.8 (dt, $^1J_{CF}=267.9$ Hz, $^2J_{CF}=37.3$ Hz; CF-CF_2,), 159.1 ppm; IR (neat): $\tilde{\nu}=1500$, 1600 (Ar), 1700 cm^{-1} (C=C); HRMS (ESI): m/z calcd for $C_{35}H_{43}F_3NaO_2^+$: 575.3107 $[M+Na^+]$; found: 575.3097.

(Z)-4-(3-(4-*sec*-Butylphenoxy)-2,3,3-trifluoroprop-1-enyl)-4′-(pentadecyloxy)biphenyl (9l): White solid, yield 87%; $R_f=0.4$ (hexane/$CH_2Cl_2=4:1$); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=0.90$ (t, $J=7.3$ Hz, 3H; CH_3), 0.97 (t, $J=6.6$ Hz, 3H; CH_3), 1.31 (d, $J=6.8$ Hz, 3H; CH_3), 1.33–1.48 (m, 22H, CH_2), 1.55 (quin, $J=7.1$ Hz, 2H; CH_2), 1.66 (quin, $J=7.3$ Hz, 2H; CH_2), 1.88 (quin, $J=6.9$ Hz, 2H; CH_2), 2.68 (sex, $J=6.9$ Hz, 1H; $C\mathit{H}CH_3$), 4.06 (t, $J=6.4$ Hz, 2H; CH_2O), 6.51 (d, $J_{HF}=36.4$ Hz, 1H; CH=CF), 7.04 (d, $J=8.6$ Hz, 2H; Ar), 7.22–7.27 (m, 4H; Ar), 7.58–7.72 ppm (m, 6H; Ar); ^{19}F NMR (188 MHz, $CDCl_3$): $\delta=-74.2$ (d, $J=13.8$ Hz; CF_2-O), -129.5 ppm (dt, $J_{HF}=36.4$ Hz, $J=13.8$ Hz; CF=CH); ^{13}C NMR

(100 MHz, $CDCl_3$): $\delta=12.1$, 14.1, 21.8, 22.7, 26.1, 29.3, 29.4, 29.4, 29.6, 29.6, 29.7–29.7 (m), 32.0, 41.1, 68.1 (CH_2O), 110.1 (d, $J_{CF}=2.2$ Hz), 114.9, 117.5 (td, $^1J_{CF}=260.5$ Hz, $^2J_{CF}=37.3$ Hz; CF_2-CF,), 121.7, 126.7, 128.0, 128.7, 128.9 (d, $^4J_{CF}=2.2$ Hz), 129.98 (d, $^4J_{CF}=7.3$ Hz), 132.4, 141.3, 145.6, 147.7, 147.7 (dt, $^1J_{CF}=267.9$ Hz, $^2J_{CF}=37.3$ Hz; CF-CF_2,), 159.1 ppm; IR (neat): $\tilde{\nu}=1500$, 1610 (Ar), 1700 cm^{-1} (C=C); HRMS (ESI): *m/z* calcd for $C_{40}H_{53}F_3NaO_2^+$ [$M+Na^+$]: 645.3890; found: 645.3892.

Synthesis of alkanes 17 by the reaction of bromides 7 with thiophenols 10 in the presence of sodium dithionate (general procedure): In argon atmospere, a mixture of compound **7** (1 mmol), thiophenol **10** (1.1 mmol), $Na_2S_2O_4xH_2O$ (1.5 mmol, 261 mg), β-picoline (2 mmol, 186 mg), and DMF (4 mL) were stirred at room temperature for 2 days (TLC control). The reaction was quenched with hydrochloric acid (5%, 50 mL), reaction products were extracted with CH_2Cl_2 (3×30 mL). The combined extracts were dried over Na_2SO_4, volatiles were removed in vacuo and the residue was purified by column chromatography on silica gel (eluent hexane/$CH_2Cl_2=8:1$). Using this procedure alkanes **17a–f** were prepared.

Synthesis of alkanes 17 by bromide–lithium exchange followed by reaction with electrophile (general procedure): In argon atmosphere, a solution of bromide **7** (223 mg, 0.5 mmol) in dry THF (15 mL) was cooled down to (−100 °C) and *t*BuLi (0.73 mL, 1.5 M in hexanes, 1.1 mmol) was added dropwise through a syringe at stirring. After stirring for 2 h at −95 °C, the solution of corresponding disulfide **16** or symmetrical thiosulfonic S-ether **18** in THF (1 mL) was rapidly added at −95–−90 °C. The reaction mixture was stirred for 1 h at −90 °C, then 1 h at −80 °C and allowed to warm slowly to room temperature. The reaction was quenched with hydrochloric acid (5%, 50 mL) and the reaction products were extracted with CH_2Cl_2 (3×30 mL). The combined extracts were dried over Na_2SO_4, volatiles were removed in vacuo and the residue was purified by column chromatography on silica gel (eluent hexane/$CH_2Cl_2=8:1$). By using this procedure alkanes **17b** and **17e–l** were prepared.

3-(4′-Butoxybiphenyl-4-yl)-1,1,2,2-tetrafluoropropyl)(*p*-tolyl)sulfane (17a): White solid, yield 68%, $R_f=0.3$ (hexane/$CH_2Cl_2=8:1$); m.p. 110.7–112.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=1.03$ (t, $J=6.95$ Hz, 3H; CH_3), 1.55 (quin, $J=7.0$ Hz, 2H; CH_2), 1.82 (quin, $J=6.9$ Hz, 2H; CH_2), 2.42 (s, 3H; CH_3), 3.41 (t, $J_{HF}=18.4$ Hz, 2H; CH_2-CF_2), 4.04 (t, $J=6.08$ Hz, 2H; CH_2O), 7.00 (d, $J=7.83$ Hz; 2H; Ar), 7.25 (d, $J=7.07$ Hz, 2H; Ar), 7.37 (d, $J=7.07$ Hz, 2H; Ar), 7.47–7.63 ppm (m, 6H; Ar); ^{19}F NMR (377 MHz, $CDCl_3$): $\delta=-88.0$ (t, $J=3.4$ Hz; CF_2-S), −110.6 ppm (tt, $J_{H\text{-}F}=18.4$ Hz, $J=3.4$ Hz; CF_2-CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=13.8$, 19.2, 21.2, 31.3, 36.9 (t, $^2J_{CF}=22.7$ Hz; CH_2CF_2,), 67.7 (CH_2O), 114.8, 117.7 (tt, $^1J_{CF}=253.2$ Hz, $^2J_{CF}=32.9$ Hz; CF_2), 120.4, 124.5 (tt, $^1J_{CF}=252.5$ Hz, $^2J_{CF}=36.6$ Hz; CF_2), 126.6, 128.0, 128.5, 130.0, 131.1, 132.8, 137.1, 140.3, 140.9, 158.8 ppm; HRMS (ESI): *m/z* calcd for $C_{26}H_{26}F_4NaOS^+$ [$M+Na^+$]: 485.1533; found: 485.1533.

(1,1,2,2-Tetrafluoro-3-(4′-(hexyloxy)biphenyl-4-yl)propyl)(*p*-tolyl)sulfane (17b): White solid, yield 65%; $R_f=0.3$ (hexane/$CH_2Cl_2=8:1$); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=0.95$ (t, $J=6.6$ Hz, 3H; CH_3), 1.35–1.43 (m, 4H; CH_2), 1.51 (quin, $J=7.0$ Hz, 2H; CH_2), 1.84 (quin, $J=7.0$ Hz, 2H; CH_2), 2.42 (s, 3H; CH_3), 3.41 (t, $J_{HF}=18.6$ Hz, 2H; CH_2-CF_2), 4.03 (t, $J=6.6$ Hz, 2H; CH_2O), 6.99 (d, $J=8.6$ Hz, 2H; Ar), 7.24 (d, $J=8.1$ Hz, 2H; Ar), 7.36 (d, $J=7.8$ Hz, 2H; Ar), 7.52–7.60 ppm (m, 6H; Ar); ^{19}F NMR (377 MHz, $CDCl_3$): $\delta=-88.1$ (t, $J=3.6$ Hz; CF_2-S), −110.8 ppm (tt, $J_{H\text{-}F}=18.6$ Hz, $J=3.6$ Hz; CF_2-CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=14.2$, 21.4, 22.7, 25.9, 29.4, 31.7, 37.0 (t, $^2J_{CF}=23.4$ Hz; CH_2CF_2), 68.1 (CH_2O), 114.9, 117.8 (tt, $^1J_{CF}=253.2$ Hz, $^2J_{CF}=32.2$ Hz; CF_2), 120.5, 124.6 (tt, $^1J_{CF}=286.9$ Hz, $^2J_{CF}=35.1$ Hz; CF_2), 126.7, 128.1, 128.7, 130.1, 131.3, 133.0, 137.2, 140.5, 141.0, 158.9 ppm; HRMS (ESI): *m/z* calcd for $C_{28}H_{30}F_4NaOS^+$: 513.1846 [$M+Na^+$]; found: 513.1853.

(3-(4′-(Decyloxy)biphenyl-4-yl)-1,1,2,2-tetrafluoropropyl)(*p*-tolyl)sulfane (17c): White solid, yield 73%; $R_f=0.4$ (hexane/$CH_2Cl_2=8:1$); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=0.93$ (t, $J=6.6$ Hz, 3H; CH_3), 1.27–1.43 (m, 12H; CH_2), 1.51 (quin, $J=7.1$ Hz, 2H; CH_2), 1.83 (quin, $J=7.0$ Hz, 2H; CH_2), 2.42 (s, 3H; CH_3), 3.41 (t, $J_{HF}=18.7$ Hz, 2H; CH_2-CF_2), 4.03 (t, $J=6.57$ Hz, 2H; CH_2O), 7.00 (d, $J=8.84$ Hz, 2H; Ar), 7.25 (d, $J=7.83$ Hz, 2H; Ar), 7.37 (d, $J=8.08$ Hz, 2H; Ar), 7.52–7.62 ppm (m, 6H; Ar); ^{19}F NMR (377 MHz, $CDCl_3$): $\delta=-88.1$ (t, $J=3.7$ Hz; CF_2-S), −110.8 ppm (tt, $J_{H\text{-}F}=18.7$ Hz, $J=3.6$ Hz; CF_2-CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=14.0$, 21.1, 22.6, 26.0, 29.2, 29.3, 29.4, 29.5, 29.6, 31.8, 36.8 (t, $^2J_{CF}=22.8$ Hz; CH_2CF_2,), 67.9 (CH_2O), 114.6, 117.6 (tt, $^1J_{CF}=252.9$ Hz, $^2J_{CF}=32.9$ Hz; CF_2), 120.3, 124.4 (tt, $^1J_{CF}=287.5$ Hz, $^2J_{CF}=37.1$ Hz; CF_2), 126.5, 127.9, 128.4, 129.9, 131.0, 132.7, 137.0, 140.2, 140.8, 158.9 ppm; HRMS (ESI): *m/z* calcd for $C_{32}H_{38}F_4NaOS^+$: 569.2472 [$M+Na^+$]; found: 569.2474.

(1,1,2,2-Tetrafluoro-3-(4′-(pentadecyloxy)biphenyl-4-yl)propyl)(*p*-tolyl)-sulfane (17d): White solid, yield 72%; $R_f=0.2$ (hexane/$CH_2Cl_2=8:1$); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=0.91$ (t, $J=6.69$ Hz, 3H; CH_3), 1.26–1,43 (m, 22H; CH_2), 1.51 (quin, $J=7.2$ Hz, 2H; CH_2), 1.83 (quin, $J=7.0$ Hz, 2H; CH_2), 2.42 (s, 3H; CH_3), 3.41 (t, $J_{HF}=18.7$ Hz, 2H; CH_2-CF_2), 4.02 (t, $J=6.6$ Hz, 2H; CH_2O), 6.99 (d, $J=8.8$ Hz, 2H; Ar), 7.24 (d, $J=7.8$ Hz, 2H; Ar), 7.36 (d, $J=8.1$ Hz, 2H; Ar), 7.52–7.59 ppm (m, 6H; Ar); ^{19}F NMR (188 MHz, $CDCl_3$): $\delta=-88.6$ (t, $J=4.0$ Hz; CF_2-S), −111.2 ppm (tt, $J_{HF}=18.7$ Hz, $J=4.0$ Hz; CF_2-CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=14.1$, 21.2, 22.7, 26.1, 29.3, 29.4, 29.5, 29.6–29.7 (m, 7CH_2), 31.9, 36.9 (t, $^2J_{CF}=23.4$ Hz; CH_2CF_2,), 68.0 (CH_2O), 114.8, 117.7 (tt, $^1J_{CF}=252.5$ Hz, $^2J_{CF}=32.2$ Hz; CF_2), 120.5, 124.5 (tt, $^1J_{CF}=288.6$ Hz, $^2J_{CF}=36.6$ Hz; CF_2), 126.6, 128.0, 128.5, 130.0, 131.1, 132.8, 137.1, 140.3, 140.9, 158.8 ppm; HRMS (ESI): *m/z* calcd for $C_{37}H_{48}F_4NaOS^+$: 639.3260 [$M+Na^+$]; found: 639.3256.

Phenyl(1,1,2,2-tetrafluoro-3-(4′-(hexyloxy)biphenyl-4-yl)propyl)sulfane (17e): White solid, yield 63%; $R_f=0.3$ (hexane/$CH_2Cl_2=8:1$); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=0.98$ (t, $J=6.6$ Hz, 3H; CH_3), 1.38–1.46 (m, 4H; CH_2), 1.54 (quin, $J=7.0$ Hz, 2H; CH_2), 1.86 (quin, $J=7.3$ Hz, 2H; CH_2), 3.44 (t, $J_{HF}=18.6$ Hz, 2H, CH_2-CF_2), 4.05 (t, $J=6.4$ Hz, 2H; CH_2O), 7.02 (d, $J=8.6$ Hz, 2H; Ar), 7.39 (d, $J=7.8$ Hz, 2H; Ar), 7.42–7.28 (m, 2H; Ar), 7.52 (t, $J=7.3$ Hz, 1H; Ar), 7.55–7.61 (m, 4H; Ar), 7.73 ppm (d, $J=8.1$ Hz, 2H, Ar); ^{19}F NMR (282 MHz, $CDCl_3$): $\delta=-88.4$ (s; CF_2-S), −111.4 ppm (t, $J_{HF}=19.1$ Hz; CF_2-CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=14.1$, 22.7, 25.8, 29.3, 31.7, 37.0 (t, $^2J_{CF}=23.5$ Hz; CH_2CF_2,), 68.1 (CH_2O), 114.9, 117.7 (tt, $^1J_{CF}=252.9$ Hz, $^2J_{CF}=32.2$ Hz; CF_2), 124.1, 124.7 (tt,, $^1J_{CF}=287.0$ Hz, $^2J_{CF}=35.2$ Hz; CF_2), 126.7, 128.1, 128.6, 129.3, 130.5, 131.2, 132.9, 137.2, 140.5, 158.9 ppm; HRMS (ESI): *m/z* calcd for $C_{28}H_{30}F_4NaOS^+$: 477.1870 [$M+Na^+$]; found: 477.1869.

(4-Methoxyphenyl)(1,1,2,2-tetrafluoro-3-(4′-(hexyloxy)biphenyl-4-yl)propyl)sulfane (17f): White solid, yield 66%; $R_f=0.3$ (hexane/$CH_2Cl_2=4:1$); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=0.94$ (t, $J=6.6$ Hz, 3H; CH_3,), 1.35–1.43 (m, 4H; CH_2), 1.50 (quin, $J=7.4$ Hz, 2H; CH_2), 1.82 (quin, $J=7.1$ Hz, 2H; CH_2), 3.39 (t, $J_{HF}=18.6$ Hz, 2H; CH_2-CF_2,), 3.84 (s, 3H; OCH_3), 4.01 (t, $J=6.6$ Hz, 2H; CH_2O), 6.94 (d, $J=8.8$ Hz, 2H; Ar), 6.98 (d, $J=8.8$ Hz, 2H; Ar), 7.35 (d, $J=8.1$ Hz, 2H; Ar), 7.51–7.56 (m, 4H; Ar), 7.59 ppm (d, $J=8.8$ Hz, 2H; Ar); ^{19}F NMR (282 MHz, $CDCl_3$): $\delta=-89.4$ (s, CF_2-S), −111.5 ppm (t, $J_{HF}=19.1$ Hz, CF_2-CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=14.1$, 22.6, 25.7, 29.7, 31.6, 37.0 (t, $^2J_{CF}=22.7$ Hz; CH_2CF_2), 55.4 (CH_3O), 68.1 (CH_2O), 114.1, 114.8, 117.7 (tt, $^1J_{CF}=253.2$ Hz, $^2J_{CF}=32.2$ Hz; CF_2), 124.4 (tt, $^1J_{CF}=286.9$ Hz, $^2J_{CF}=35.1$ Hz; CF_2), 126.7, 128.0, 128.6, 131.2, 132.9, 138.9, 139.3, 140.4, 158.9, 161.6 ppm; HRMS (ESI): *m/z* calcd for $C_{28}H_{34}F_4NO_2S^+$: 524.2241 [M^+]; found: 524.2243.

Methyl(1,1,2,2-tetrafluoro-3-(4′-(hexyloxy)biphenyl-4-yl)propyl)sulfane (17g): White solid, yield 47%; $R_f=0.3$ (hexane/$CH_2Cl_2=8:1$); m.p. 80–82 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=0.96$ (t, $J=6.7$ Hz, 3H; CH_3), 1.35–1.44 (m, 4H; CH_2), 1.52 (quin, $J=7.1$ Hz, 2H; CH_2), 1.85 (quin, $J=7.0$ Hz, 2H; CH_2), 2.42 (s, 3H; SCH_3), 3.41 (t, $J_{HF}=19.1$ Hz, 2H; CH_2-CF_2,), 4.03 (t, $J=6.6$ Hz, 2H; CH_2O,), 7.01 (d, $J=8.6$ Hz, 2H; Ar), 7.38 (d, $J=7.8$ Hz, 2H, Ar), 7.53–7.59 ppm (m, 4H; Ar); ^{19}F NMR (282 MHz, $CDCl_3$): $\delta=-92.7$ (s, CF_2-S), −112.3 ppm (t, $J_{HF}=19.1$ Hz, CF_2-CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=10.2$, 14.1, 22.7, 25.8, 29.3, 31.7, 36.9 (t, $^2J_{CF}=23.2$ Hz; CH_2CF_2,), 68.1 (CH_2O), 114.8, 117.7 (tt, $^1J_{CF}=251.2$ Hz, $^2J_{CF}=32.9$ Hz; CF_2), 126.7, 128.1, 128.6, 131.2, 132.9, 140.4, 158.9 ppm; HRMS (ESI): *m/z* calcd for $C_{22}H_{27}F_4OS^+$: 415.1713 [$M+H^+$]; found: 415.1713.

Butyl(1,1,2,2-tetrafluoro-3-(4′-(hexyloxy)biphenyl-4-yl)propyl)sulfane (17h): White solid, yield 53%; $R_f=0.3$ (hexane/$CH_2Cl_2=8:1$); m.p. 70–72 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=0.92$–1.01 (m, 6H; CH_3), 1.37–1.43 (m, 4H; CH_2), 1.46–1.55 (m, 4H; CH_2), 1.73 (quin, $J=7.5$ Hz, 2H; CH_2), 1.84 (quin, $J=7.0$ Hz, 2H; CH_2), 2.97 (t, $J=7.4$ Hz, 2H; SCH_2,), 3.40 (t, $J_{HF}=18.7$ Hz, 2H; CH_2-CF_2,), 4.03 (t, $J=6.5$ Hz, 2H; CH_2O), 7.00

(d, $J=8.6$ Hz, 2H; Ar), 7.37 (d, $J=7.8$ Hz, 2H; Ar), 7.53–7.60 ppm (m, 4H; Ar); ^{19}F NMR (282 MHz, $CDCl_3$): $\delta=-89.8$ (s; CF_2-S), −112.5 ppm (t, $J_{HF}=19.1$ Hz; CF_2-CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=13.5$, 14.1, 21.9, 22.7, 25.8, 27.8, 29.3, 29.8, 31.7, 37.0 (t, $^2J_{CF}=22.7$ Hz; CH_2CF_2,), 68.1 (CH_2O), 114.8, 117.6 (tt, $^1J_{CF}=252.5$ Hz, $^2J_{CF}=32.2$ Hz; CF_2), 126.7, 128.1, 128.7, 131.2, 133.0, 140.4, 158.9 ppm; HRMS (ESI): *m*/*z* calcd for $C_{25}H_{32}F_4NaOS^+$: 479.2002 [$M+Na^+$]; found: 479.2001.

Naphthalen-2-yl(1,1,2,2-tetrafluoro-3-(4′-(hexyloxy)biphenyl-4-yl)propyl)sulfane (17i): White solid, yield 63%; $R_f=0.3$ (hexane/CH_2Cl_2=8:1); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=0.96$ (t, $J=6.6$ Hz, 3H; CH_3,), 1.35–1.44 (m, 4H; CH_2), 1.52 (quin, $J=7.1$ Hz, 2H; CH_2), 1.85 (quin, $J=7.0$ Hz, 2H; CH_2), 3.45 (t, $J_{HF}=18.6$ Hz; 2H; CH_2-CF_2), 4.03 (t, $J=6.6$ Hz; 2H, CH_2O), 7.01 (d, $J=8.8$ Hz, 2H; Ar), 7.38 (d, $J=8.1$ Hz, 2H; Ar), 7.54–7.62 (m, 6H; Ar), 7.73 (d, $J=8.6$ Hz; 1H; Ar), 7.88–7.92 (m, 3H; Ar), 8.25 ppm (s, 1H; Ar); ^{19}F NMR (282 MHz, $CDCl_3$): $\delta=-88.2$ (s; CF_2-S), −111.2 ppm (t, $J_{HF}=19.1$ Hz; CF_2-CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=14.1$, 22.7, 25.8, 29.4, 31.7, 37.0 (t, $^2J_{CF}=22.7$ Hz; CH_2CF_2,), 68.1 (CH_2O), 114.9, 117.8 (tt, $^1J_{CF}=252.5$ Hz, $^2J_{CF}=32.5$ Hz; CF_2), 121.4, 124.9 (tt, $^1J_{CF}=287.0$ Hz, $^2J_{CF}=36.6$ Hz; CF_2), 126.8, 126.9, 127.8, 127.8, 128.1, 128.2, 128.6, 128.9, 131.3, 132.9, 132.9, 133.5, 133.9, 137.8, 140.5, 158.9 ppm; HRMS (ESI): *m*/*z* calcd for $C_{31}H_{34}F_4NOS^+$: 544.2292 [$M+NH_4^+$]; found: 544.2285.

(4-isoPropylphenyl)(1,1,2,2-tetrafluoro-3-(4′-(hexyloxy)biphenyl-4-yl)propyl)sulfane (17j): White solid, yield 52%; $R_f=0.3$ (hexane/CH_2Cl_2=8:1); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=0.94$ (t, $J=6.6$ Hz, 3H; CH_3), 1.29 (d, $J=6.9$ Hz, 6H; -CH(CH_3)$_2$), 1.36–1.41 (m, 4H; CH_2), 1.50 (quin, $J=7.0$ Hz, 2H; CH_2), 1.83 (quin, $J=6.8$ Hz, 2H; CH_2), 2.96 (quintet, $J=6.9$ Hz, 1H; -CH(CH_3)$_2$), 3.41 (t, $J_{HF}=18.5$ Hz, 2H; CH_2-CF_2), 4.02 (t, $J=6.6$ Hz, 2H; CH_2O), 6.99 (d, $J=8.8$ Hz, 2H; Ar), 7.28 (d, $J=8.0$ Hz, 2H; Ar), 7.36 (d, $J=8.0$ Hz, 2H; Ar), 7.52–7.58 (m, 4H; Ar), 7.60 ppm (d, $J=8.0$ Hz, 2H; Ar); ^{19}F NMR (282 MHz, $CDCl_3$): $\delta=-88.7$ (s, CF_2-S), −111.5 ppm (t, $J_{HF}=19.1$ Hz, CF_2-CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=14.0$, 22.6, 23.7, 25.7, 29.3, 31.6, 33.9, 36.9 (t, $^2J_{CF}=22.9$ Hz; CH_2CF_2,), 68.1 (CH_2O), 114.8, 117.7 (CF_2), 120.7, 126.7, 127.4, 128.0, 128.6, 131.2, 132.9, 137.2, 140.4, 151.6, 158.8 ppm; HRMS (ESI): *m*/*z* calcd for $C_{30}H_{35}F_4OS^+$: 519.2339 [$M+H^+$]; found: 519.2327.

Mesityl(1,1,2,2-tetrafluoro-3-(4′-(hexyloxy)biphenyl-4-yl)propyl)sulfane (17k): White solid, yield 53%; $R_f=0.3$ (hexane/CH_2Cl_2=8:1); m.p. 103.2–105.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=0.99$ (t, $J=6.6$ Hz, 3H; CH_3), 1.39–1.45 (m, 4H; CH_2), 1.54 (quin, $J=7.2$ Hz, 2H; CH_2), 1.86 (quin, $J=7.0$ Hz, 2H; CH_2), 2.35 (s, 3H; CH_3), 2.59 (s, 6H; CH_3), 3.46 (t, $J_{HF}=18.6$ Hz, 2H; CH_2-CF_2,), 4.03 (t, $J=6.6$ Hz, 2H; CH_2O,), 7.02 (d, $J=8.8$ Hz, 2H; Ar,), 7.06 (m, 2H), 7.41 (d, $J=8.1$ Hz, 2H; Ar), 7.55–7.60 ppm (m, 4H; Ar); ^{19}F NMR (282 MHz, $CDCl_3$): $\delta=-87.7$ (s; CF_2-S), −112.0 ppm (t, $J_{HF}=19.1$ Hz; CF_2-CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=14.0$, 21.1, 22.3, 22.6, 25.7, 29.7, 31.6, 36.8 (t, CH_2CF_2, $^2J_{CF}=22.9$ Hz), 68.0 (CH_2O), 114.8, 117.6 (tt, $^1J_{CF}=252.5$ Hz, $^2J_{CF}=32.4$ Hz; CF_2), 119.6, 125.7 (tt, $^1J_{CF}=289.0$ Hz, $^2J_{CF}=36.1$ Hz; CF_2), 126.6, 128.0, 128.6, 129.4, 131.2, 132.9, 140.3, 140.8, 145.7, 158.8 ppm; HRMS (ESI): *m*/*z* calcd for $C_{30}H_{38}F_4NOS^+$: 536.2605 [$M+NH_4^+$]; found: 536.2585.

(4-Fluorophenyl)(1,1,2,2-tetrafluoro-3-(4′-(hexyloxy)biphenyl-4-yl)propyl)sulfane (17l): White solid, yield 46%; $R_f=0.3$ (hexane/CH_2Cl_2=8:1); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=0.95$ (t, $J=6.6$ Hz, 3H; CH_3), 1.35–1.43 (m, 4H; CH_2), 1.51 (quin, $J=7.2$ Hz, 2H; CH_2), 1.83 (quin, $J=7.1$ Hz, 2H; CH_2), 3.40 (t, $J_{HF}=18.6$ Hz, 2H; CH_2-CF_2,), 4.02 (t, $J=6.6$ Hz, 2H; CH_2O), 6.99 (d, $J=8.8$ Hz, 2H; Ar), 7.12 (t, $^3J_{HF}=8.6$ Hz, $J=8.8$ Hz, 2H; Ar), 7.36 (d, $J=8.3$ Hz, 2H; Ar), 7.52–7.58 (m, 4H; Ar), 7.65–7.69 ppm (dd, $^4J_{HF}=5.3$ Hz, $J=8.8$ Hz, 2H; Ar); ^{19}F NMR (282 MHz, $CDCl_3$): $\delta=-88.8$ (s; CF_2-S), −110.29–110.18 (m; -C_6H_4-F), −111.2 ppm (t, $J_{HF}=19.1$ Hz; CF_2-CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=14.0$, 22.6, 25.8, 29.3, 31.6, 36.9 (t, $^2J_{CF}=22.9$ Hz; CH_2CF_2), 68.1 (CH_2O), 114.8, 116.5 (d, $^2J_{CF}=22.1$ Hz; Ar), 117.7 (tt, $^1J_{CF}=252.9$ Hz, $^2J_{CF}=32.2$ Hz; CF_2), 119.3, 124.4 (tt, $^1J_{CF}=288.2$ Hz, $^2J_{CF}=35.1$ Hz; CF_2), 126.7, 128.0, 128.4, 131.2, 132.9, 139.4 (d, $^3J_{CF}=8.9$ Hz; Ar), 140.5, 158.9, 164.4 ppm (d, $^1J_{CF}=251.7$ Hz; Ar); HRMS (ESI): *m*/*z* calcd for $C_{27}H_{28}F_5OS^+$: 495.1776 [$M+H^+$]; found: 495.1769.

(1,1,2,2-Tetrafluoro-3-(4′-(octadecyloxy)biphenyl-4-yl)propyl)(*p*-tolyl)sulfane (17m): White solid, yield 74%, $R_f=0.2$ (hexane/CH_2Cl_2=8:1); m.p. 89.5–90.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=0.91$ (t, $J=6.7$ Hz, 3H; CH_3), 1.26–1.43 (m, 28H; CH_2), 1.50 (quin, $J=7.1$ Hz, 2H; CH_2), 1.83 (quin, $J=7.0$ Hz, 2H; CH_2), 2.41 (s, 3H; CH_3), 3.40 (t, $J_{HF}=18.6$ Hz, 2H; CH_2-CF_2), 4.02 (t, $J=6.4$ Hz, 2H; CH_2O), 6.99 (d, $J=8.8$ Hz, 2H; Ar), 7.24 (d, $J=7.8$ Hz, 2H; Ar), 7.36 (d, $J=8.1$ Hz, 2H; Ar), 7.51–7.60 ppm (m, 6H; Ar); ^{19}F NMR (188 MHz, $CDCl_3$): $\delta=-88.6$ (t, $J=4.0$ Hz; CF_2-S), −111.2 ppm (tt, $J_{HF}=18.6$ Hz, $J=4.0$ Hz; CF_2-CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=14.2$, 21.3, 22.8, 26.2, 29.5, 29.6, 29.7–30.00 (m, 11CH_2), 32.1, 37.1 (t, $^2J_{CF}=22.7$ Hz; CH_2CF_2,), 68.1 (CH_2O), 114.9, 117.8 (tt, $^1J_{CF}=254.6$ Hz, $^2J_{CF}=31.2$ Hz; CF_2), 120.6, 124.7 (tt, $^1J_{CF}=287.5$ Hz, $^2J_{CF}=35.4$ Hz; CF_2), 126.7, 128.1, 128.7, 130.1, 131.3, 132.94, 137.2, 140.5, 141.0, 159.0 ppm; HRMS (ESI): *m*/*z* calcd for $C_{40}H_{54}F_4NaOS^+$: 681.3724 [$M+Na^+$]; found: 681.3721.

Synthesis of (2-bromo-1,1,2,2-tetrafluoroethyl)(*p*-tolyl)sulfane (20): 4-Methyl-thiophenol (44.2 g, 0.36 mol) in DMF (100 mL) was slowly added to a suspension of sodium hydride (28 g, 60% in oil, 0.70 mol) in anhydrous DMF (200 mL) at 0 °C within 45 min. The reaction mixture was cooled to −50 °C and 1,2-dibromotetrafluoroethane (53 mL, 0.45 mol) was added in 1 h. The reaction mixture was stirred at −50 °C for 3 h then warmed slowly to room temperature within 2 h. Excessive sodium hydride was quenched by dropwise addition of water (400 mL) under ice-water bath cooling. The aqueous phase was extracted with MTBE (3× 300 mL), combined organic phases were washed with water (3×300 mL), and then dried over $CaCl_2$. The solvents were evaporated in vacuo and the residue was purified by chromatography on silica gel by using hexane as an eluent. Compound **22a** was obtained as a colourless liquid (83.40 g, 76%); $R_f=0.6$ (hexane); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=2.42$ (s, 3H, CH_3), 7.25 (d, $J=8.1$ Hz, 2H, Ar), 7.56 ppm (d, $J=8.1$ Hz, 2H, Ar); spectroscopic data are in agreement with those in the literature, see ref. [15].

Synthesis of 19 and 21 by COR: A solution of 4-bromobenzaldehyde (20 mmol) in EtOH (40 mL) was added dropwise to a solution of hydrazine hydrate (1.2 mL, 20 mmol) in EtOH (20 mL) under stirring. The reaction mixture was stirred until aldehyde disappeared (overnight, TLC monitoring). Then 1,2-ethylenediamine (3.0 mL, 44 mmol) and freshly purified CuCl (200 mg, 2 mmol) were added. After 10 min (2-bromo-1,1,2,2-tetrafluoroethyl)(*p*-tolyl)sulfane **20** (22 mmol) was added dropwise at room temperature. Next, the reaction mixture was stirred for 5 h at 45 °C. (In case of one pot synthesis of **21**, at this step 5 M NaOH solution in water (10 mL, 50 mmol) was added and reaction mixture was heated at reflux for 4 h). Diluted hydrochloric acid (5%, 300 mL) was added, reaction products were extracted with CH_2Cl_2 (3×100 mL). The combined extracts were dried over Na_2SO_4, volatiles removed in vacuo, and the residue was purified by column chromatography on silica gel.

(3-(4-Bromophenyl)-1,1,2,2-tetrafluoropropyl)(*p*-tolyl)sulfane (19): White solid, yield 29%; $R_f=0.6$ (hexane); m.p. 89.2–91.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=2.41$ (s, 3H; CH_3), 3.34 (t, $J=18.3$ Hz, 2H; CH_2-CF_2), 7.19 (d, $J=8.3$ Hz, 2H; Ar), 7.24 (d, $J=8.1$ Hz, 2H; Ar), 7.50 (d, $J=8.3$ Hz; 2H, Ar), 7.56 ppm (d, $J=8.1$ Hz; 2H, Ar); ^{19}F NMR (377 MHz, $CDCl_3$): $\delta=-88.03$ (t, $J=3.4$ Hz; CF_2S), −110.65 ppm (tt, $J_{HF}=18.3$ Hz, $J=3.4$ Hz; CF_2-CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=21.3$, 36.7 (t, $^2J_{CF}=22.7$ Hz; CH_2CF_2), 117.3 (tt, CF_2, $^1J_{CF}=253.2$ Hz, $^2J_{CF}=32.9$ Hz), 120.2, 122.0, 124.4 (tt, CF_2, $^1J_{CF}=287.6$ Hz, $^2J_{CF}=35.9$ Hz), 129.3, 130.0, 131.6, 132.4, 137.1, 141.0 ppm; elemental analysis calcd (%) for $C_{16}H_{13}BrF_4S$: C 48.81, H 3.24; found: C 48.87, H, 3.33. Alternatively compound **19** was prepared in 60% yield by using the procedure for the transformation of bromides **7** into alkanes **17** by the reaction with thiophenols **10** in the presence of sodium dithionite.

(3-(4-Bromophenyl)-1,1,2-trifluoroallyl)(*p*-tolyl)sulfane (21): Obtained as a mixture of *Z*/*E* isomers (96:4); white solid, yield 23% (39% one pot); $R_f=0.7$ (hexane); m.p. 73.6–74.8 °C; *Z*-isomer: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=2.38$ (s, 3H; CH_3), 5.97 (d, $J_{HF}=35.5$ Hz, 1H; CH=CF), 7.19 (d, $J=7.8$ Hz, 2H; Ar), 7.34 (d, $J=8.3$ Hz, 2H; Ar), 7.48–7.55 ppm (m, 4H; Ar); ^{19}F NMR (377 MHz, $CDCl_3$): $\delta=-80.3$ (d, $J=19.4$ Hz; CF_2-S), −123.1 ppm (dt, $J_{HF}=35.5$ Hz, $J=19.4$ Hz; CF=CH); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=21.2$, 109.3, 122.3, 122.8 (td, CF_2-CF, $^1J_{CF}=278.2$ Hz, $^2J_{CF}=38.8$ Hz), 123.1, 130.0, 130.8 (d, $J_{CF}=6.8$ Hz), 131.8, 132.4, 136.7, 140.9, 149.4 ppm (dt, CF-CF_2, $^1J_{CF}=267.3$ Hz, $^2J_{CF}=30.4$ Hz); *E*-isomer: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=6.53$ (d, $J=21.2$ Hz, 1H; CH=

CF,), 7.24 ppm (d, $J=7.8$ Hz, 2H; Ar); ^{19}F NMR (377 MHz, $CDCl_3$): $\delta=-76.0$ (d, $J=19.1$ Hz; CF_2-S), −114.8 ppm (dt, $J=21.2$ Hz, $J=19.1$ Hz; CF=CH); the other signals are identical to those of the Z isomer; IR (neat): $\tilde{\nu}=1380$, 1470, 1600, 1700 cm^{-1} (C=C); elemental analysis calcd (%) for $C_{16}H_{12}BrF_3S$: C 52.09, H 3.54; found: C 51.49, H 3.24.

Synthesis of sulfones 22 and 23 by oxidation: A mixture of corresponding sulfides **19** or **21** (10 mmol), acetic acid (20 mL) and 40% aqueous H_2O_2 (20 mL) were heated at reflux for 3 h. Next, water (60 mL) was added and the reaction mixture was cooled down to room temperature; a precipitate formed, which was filtered off and dried.

1-Bromo-4-(2,2,3,3-tetrafluoro-3-tosylpropyl)benzene (22): White solid, yield 86%, $R_f=0.5$ (hexane/CH_2Cl_2=2:1); m.p. 99.9–101.3°C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=2.52$ (s, 3H; CH_3), 3.51 (t, $J_{HF}=19.0$ Hz, 2H; CH_2-CF_2), 7.20 (d, $J=8.3$ Hz, 2H; Ar,), 7.46 (d, $J=8.3$ Hz, 2H; Ar,), 7.50 (d, $J=8.3$ Hz, 2H; Ar,), 7.92 ppm (d, $J=8.3$ Hz, 2H; Ar,); ^{19}F NMR (188 MHz, $CDCl_3$): $\delta=-110.0$ (t, $J_{H\text{-}F}=19.0$ Hz; CF_2-CH_2), −114.0 ppm (s; CF_2-SO_2); ^{13}C NMR (400 MHz, [D_6]acetone): 21.0, 36.9 (t, $J_{CF}=21.9$ Hz; CH_2-CF_2), 115.7 (tt, $^1J_{CF}=254.0$ Hz, $^2J_{CF}=35.8$ Hz; CF_2,), 117.4 (tt, $^1J_{CF}=253.5$ Hz, $^2J_{CF}=28.5$ Hz; CF_2), 121.8, 126.7, 130.1, 130.6, 130.9, 131.6, 133.0, 148.5 ppm; elemental analysis calcd (%) for $C_{16}H_{13}BrF_4O_2S$: C 45.42, H 3.12; found: C 45.19, H 3.08.

1-Bromo-4-(2,3,3-trifluoro-3-tosylprop-1-enyl)benzene (23): Obtained as a pure *Z* isomer; white solid, yield 78%, $R_f=0.5$ (hexane/CH_2Cl_2=2:1); m.p. 146.2–147.9°C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=2.53$ (s, 3H; CH_3), 6.37 (d, $J_{HF}=35.4$ Hz, 1H; CH=CF,), 7.45–7.48 (m, 4H; Ar), 7.56 (d, $J=8.6$ Hz, 2H; Ar,), 7.93 ppm (d, $J=8.1$ Hz, 2H; Ar,); ^{19}F NMR (188 MHz, $CDCl_3$): $\delta=-108.3$ (t, $J_{H\text{-}F}=15.5$ Hz; CF_2-SO_2), −124.3 ppm (dt, $J_{HF}=35.4$ Hz, $J=15.5$ Hz; CF=CH); ^{13}C NMR (400 MHz, [D_6]acetone): 20.9, 114.8, 123.0 (td, CF_2-CF, $^1J_{CF}=278.1$ Hz, $^2J_{CF}=38.8$ Hz), 123.3, 129.2, 130.6, 130.8, 131.7 (d, $J_{CF}=7.3$ Hz), 132.2, 133.0, 148.2, 149.6 ppm (dt, CF-CF_2, $^1J_{CF}=267.2$ Hz, $^2J_{CF}=30.7$ Hz); IR (neat): $\tilde{\nu}=1490$, 1690 cm^{-1} (C=C); elemental analysis calcd (%) for $C_{16}H_{12}BrF_3O_2S$: C 47.51, H 3.24; found: C 47.42, H 2.98.

Suzuki coupling of bromides 5a, 19, 21, 22, and 23 with boronic acids 6 (general procedure): A round bottomed flask (100 mL) was charged with corresponding boronic acid **6** (1.05 mmol), aryl bromide **5a**, **19**, **21–23** (1 mmol), 1,2-dimethoxyethane (30 mL) under argon flow. Next, Pd-$(PPh_3)_4$ (58 mg, 0.05 mmol) and solution of K_2CO_3 (830 mg, 6 mmol) in water (2.5 mL) were added. The reaction mixture was heated at reflux for 4–6 h (TLC control). Solvent was evaporated and the residue was quenched with 1 M solution of HCl in water. The aqueous phase was extracted with CH_2Cl_2 (3×30 mL), the combined organic layers were washed with water (3×30 mL) and dried over Na_2SO_4. Solvent evaporation left a crude product that was purified by column chromatography on silica gel (eluent hexane/CH_2Cl_2=8:1 or 2:1).

4-(3-Bromo-2,2,3,3-tetrafluoropropyl)-4′-butoxybiphenyl (7a): White solid, yield 73%; $R_f=0.2$ (hexane/CH_2Cl_2=8:1); m.p. 77.1–78.9°C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=1.02$ (t, $J=7.3$ Hz, 3H; CH_3), 1.53 (quin, $J=7.3$ Hz, 2H; CH_2), 1.82 (quin, $J=7.0$ Hz, 2H; CH_2), 3.43 (t, $J_{HF}=18.3$ Hz, 2H; CH_2-CF_2), 4.03 (t, $J=6.4$ Hz, 2H; CH_2O), 7.00 (d, $J=8.9$ Hz, 2H; Ar), 7.36 (d, $J=8.1$ Hz, 2H; Ar), 7.52–7.58 ppm (m, 4H; Ar); ^{19}F NMR (188 MHz, $CDCl_3$): $\delta=-65.5$ (t, $J=4.0$ Hz; CF_2-Br), −111.0 ppm (tt, $J_{H\text{-}F}=18.3$ Hz, $J=4.0$ Hz; CF_2-CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=13.8$, 19.2, 31.3, 36.3 (t, $^2J_{CF}=22.7$ Hz; CH_2CF_2,), 67.7 (CH_2O), 114.8, 116.0 (tt, $^1J_{CF}=254.7$ Hz, $^2J_{CF}=31.5$ Hz; CF_2), 124.6 (tt, CF_2, $^1J_{CF}=272.3$ Hz, $^2J_{CF}=40.3$ Hz), 126.8, 127.7, 128.0, 131.1, 132.7, 140.7, 158.9 ppm; HRMS (ESI): m/z calcd for $C_{19}H_{19}BrF_4NaO^+$: 419.0628 $[M+H^+]$; found: 419.0611.

4-(3-Bromo-2,2,3,3-tetrafluoropropyl)-4′-(hexyloxy)biphenyl (7b): White solid, yield 94%; $R_f=0.3$ (hexane/CH_2Cl_2=8:1); m.p. 53.8–55.6°C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=0.98$ (t, $J=7.2$ Hz, 3H, CH_3,), 1.37–1.45 (m, 4H; CH_2), 1.54 (quin, $J=6.8$ Hz, 2H; CH_2), 1.86 (quin, $J=7.1$ Hz, 2H; CH_2), 3.44 (t, $J_{HF}=18.2$ Hz, 2H; CH_2-CF_2), 4.04 (t, $J=6.4$ Hz, 2H; CH_2O), 7.02 (d, $J=8.6$ Hz, 2H; Ar), 7.38 (d, $J=7.8$ Hz, 2H; Ar,), 7.55–7.61 ppm (m, 4H; Ar); ^{19}F NMR (188 MHz, $CDCl_3$): $\delta=-65.5$ (t, $J=4.0$ Hz; CF_2-Br), −111.0 ppm (tt, $J_{HF}=19.2$ Hz, $J=4.0$ Hz; CF_2-CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=14.0$, 22.6, 25.7, 29.3, 31.6, 36.3 (t, $^2J_{CF}=22.7$ Hz; CH_2CF_2,), 68.0 (CH_2O), 114.8, 116.0 (tt, $^1J_{CF}=254.0$ Hz, $^2J_{CF}=31.1$ Hz; CF_2), 117.8 (tt, $^1J_{CF}=311.8$ Hz, $^2J_{CF}=39.5$ Hz; CF_2), 126.7, 127.7, 128.0, 131.1, 132.7, 140.6, 158.9 ppm; HRMS (ESI): m/z calcd for $C_{21}H_{24}BrF_4O^+$: 447.0941 $[M+H^+]$; found: 447.0944.

4-(3-Bromo-2,2,3,3-tetrafluoropropyl)-4′-(decyloxy)biphenyl (7c): White solid, yield 82%; $R_f=0.3$ (hexane/CH_2Cl_2=8:1); m.p. 62.3–64.4°C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=0.93$ (t, $J=7.3$ Hz, 3H; CH_3), 1.37–1.45 (m, 12H; CH_2), 1.50 (quin, $J=7.1$ Hz, 2H; CH_2), 1.84 (quin, $J=7.0$ Hz, 2H; CH_2), 3.43 (t, $J_{HF}=18.2$ Hz, 2H, CH_2-CF_2), 4.02 (t, $J=6.6$ Hz, 2H; CH_2O), 7.00 (d, $J=8.8$ Hz, 2H; Ar), 7.36 (d, $J=7.3$ Hz, 2H; Ar), 7.52–7.59 ppm (m, 4H; Ar); ^{19}F NMR (188 MHz, $CDCl_3$): $\delta=-65.5$ (t, $J=4.0$ Hz; CF_2-Br), −111.0 ppm (tt, $J_{HF}=18.2$ Hz, $J=4.0$ Hz; CF_2-CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=14.1$, 22.7, 26.1, 29.3, 29.4, 29.5, 25.6, 29.7, 31.9, 36.3 (t, $^2J_{CF}=22.7$ Hz; CH_2CF_2,), 68.0 (CH_2O), 114.8, 116.0 (tt, $^1J_{CF}=254.3$ Hz, $^2J_{CF}=31.3$ Hz; CF_2), 118.2 (tt, $^1J_{CF}=272.0$ Hz, $^2J_{CF}=40.2$ Hz; CF_2), 126.7, 127.7, 128.0, 131.1, 132.7, 140.6, 158.9 ppm; HRMS (ESI): m/z calcd for $C_{25}H_{31}BrF_4NaO^+$: 503.1567 $[M+H^+]$; found: 503.1567.

4-(3-Bromo-2,2,3,3-tetrafluoropropyl)-4′-(pentadecyloxy)biphenyl (7d): white solid, yield 57%; $R_f=0.4$ (hexane/CH_2Cl_2=8:1); m.p. 73.6–75.4°C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=0.92$ (t, $J=6.8$ Hz, 3H; CH_3,), 1.36–1.45 (m, 22H; CH_2), 1.51 (quin, $J=7.1$ Hz, 2H; CH_2), 1.84 (quin, $J=7.0$ Hz, 2H; CH_2), 3.43 (t, $J_{HF}=18.3$ Hz, 2H; CH_2-CF_2), 4.02 (t, $J=6.6$ Hz, 2H; CH_2O), 7.00 (d, $J=8.6$ Hz, 2H; Ar), 7.37 (d, $J=7.8$ Hz, 2H; Ar), 7.53–7.59 ppm (m, 4H; Ar); ^{19}F NMR (188 MHz, $CDCl_3$): $\delta=-65.5$ (t, $J=4.0$ Hz; CF_2-Br), −111.0 ppm (tt, $J_{H\text{-}F}=18.3$ Hz, $J=4.0$ Hz; CF_2-CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=14.1$, 22.7, 26.1, 29.3, 29.4, 29.5, 29.6, 29.7 −29.8 (m, 6CH_2), 32.0, 36.3 (t, $^2J_{CF}=22.7$ Hz; CH_2CF_2), 68.1 (CH_2O), 114.8, 116.0 (tt, $^1J_{CF}=254.0$ Hz, $^2J_{CF}=30.7$ Hz; CF_2), 117.8 (tt, $^1J_{CF}=271.5$ Hz, $^2J_{CF}=40.3$ Hz; CF_2), 126.8, 127.7, 128.0, 131.1, 132.7, 140.7, 158.9 ppm; HRMS (ESI): m/z calcd for $C_{30}H_{41}BrF_4NaO^+$: 595.2169 $[M+Na^+]$; found: 595.2151.

4-Butoxy-4′-(2,2,3,3-tetrafluoro-3-tosylpropyl)biphenyl (24a): White solid, yield 91%, $R_f=0.3$ (hexane/CH_2Cl_2=2:1); m.p. 101.3–102.8°C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=1.02$ (t, $J=7.33$ Hz, 3H; CH_3), 1.54 (quin, $J=7.3$ Hz, 2H; CH_2), 1.82 (quin, $J=6.8$ Hz, 2H; CH_2), 2.52 (s, 3H; CH_3), 3.57 (t, $J_{HF}=19.3$ Hz, 2H; CH_2-CF_2), 4.03 (t, $J=6.3$ Hz, 2H; CH_2O), 7.00 (d, $J=8.1$ Hz, 2H; Ar), 7.37 (d, $J=7.8$ Hz, 2H; Ar), 7.46 (d, $J=7.8$ Hz, 2H; Ar), 7.51–7.58 (m, 4H; Ar), 7.95 ppm (d, $J=8.1$ Hz, 2H; Ar); ^{19}F NMR (188 MHz, $CDCl_3$): $\delta=-110.0$ (t, $J=19.3$ Hz; CF_2-CH_2), −113.9 ppm (s; CF_2-SO_2);^{13}C NMR (100 MHz, $CDCl_3$): $\delta=13.8$, 19.4, 21.8, 31.3, 37.6 (t, $^2J_{CF}=21.9$ Hz; CH_2CF_2,), 67.6 (CH_2O), 114.7, 115.7 (tt, $^1J_{CF}=298.4$ Hz, $^2J_{CF}=35.4$ Hz; CF_2), 117.1 (tt, CF_2, $^1J_{CF}=255.5$ Hz, $^2J_{CF}=27.0$ Hz), 126.6, 127.5, 127.9, 129.7, 130.1, 130.8, 131.2, 132.6, 139.9, 147.6, 158.8 ppm; HRMS (ESI): m/z calcd for $C_{26}H_{26}F_4NaO_3S^+$: 517.1431 $[M+Na^+]$; found: 517.1436.

4-(Hexyloxy)-4′-(2,2,3,3-tetrafluoro-3-tosylpropyl)biphenyl (24b): White solid, yield 83%, $R_f=0.3$ (hexane/CH_2Cl_2=2:1); m.p. 106.3–107.1°C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=0.94$ (t, $J=6.2$ Hz, 3H; CH_3), 1.33–1.45 (m, 4H; CH_2), 1.50 (quin, $J=7.0$ Hz, 2H; CH_2), 1.83 (quin, $J=7.0$ Hz, 2H; CH_2), 2.52 (s, 3H; CH_3), 3.56 (t, $J_{HF}=19.2$ Hz, 2H; CH_2-CF_2), 4.02 (t, $J=6.4$ Hz, 2H; CH_2O), 7.00 (d, $J=8.3$ Hz, 2H; Ar), 7.37 (d, $J=7.6$ Hz, 2H; Ar), 7.46 (d, $J=7.6$ Hz, 2H; Ar), 7.51–7.57 (m, 4H; Ar), 7.95 ppm (d, $J=8.3$ Hz; 2H; Ar); ^{19}F NMR (188 MHz, $CDCl_3$): $\delta=-110.0$ (t, $J=19.2$ Hz; CF_2-CH_2), −113.9 ppm (s; CF_2-SO_2); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=14.0$, 21.7, 22.5, 25.7, 29.2, 31.5, 37.6 (t, $^2J_{CF}=21.9$ Hz; CH_2CF_2,), 67.9 (CH_2O), 114.7, 115.7 (tt, $^1J_{CF}=298.4$ Hz, $^2J_{CF}=34.6$ Hz; CF_2), 117.1 (tt, $^1J_{CF}=253.8$ Hz, $^2J_{CF}=27.0$ Hz; CF_2), 126.6, 127.5, 127.9, 129.7, 130.1, 130.8, 131.2, 132.6, 140.5, 147.6, 158.8 ppm; HRMS (ESI): m/z calcd for $C_{28}H_{30}F_4NaO_3S^+$: 545.1744 $[M+Na^+]$; found: 545.1749.

4-(Decyloxy)-4′-(2,2,3,3-tetrafluoro-3-tosylpropyl)biphenyl (24c): White solid, yield 86%, $R_f=0.4$ (hexane/CH_2Cl_2=2:1); m.p. 107.5–108.2°C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=0.91$ (t, $J=6.7$ Hz, 3H; CH_3), 1.24–1.39 (m, 12H; CH_2), 1.45–1.53 (m, 2H; CH_2), 1.78–1.87 (m, 2H; CH_2), 2.52 (s, 3H; CH_3), 3.56 (t, $J_{HF}=19.2$ Hz, 2H; CH_2-CF_2), 4.01 (t, $J=6.6$ Hz, 2H; CH_2O), 6.98 (d, $J=7.8$ Hz, 2H; Ar), 7.36 (d, $J=6.8$ Hz, 2H; Ar), 7.46 (d, $J=7.1$ Hz, 2H; Ar), 7.51–7.58 (m, 4H; Ar), 7.94 ppm (d, $J=7.6$ Hz, 2H; Ar); ^{19}F NMR (188 MHz, $CDCl_3$): $\delta=-110.1$ (t, $J=19.2$ Hz; CF_2-CH_2),

−113.9 ppm (s; CF_2-SO_2); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=14.0$, 21.7, 22.6, 26.0, 29.3, 29.4, 29.5, 29.7, 31.8, 37.6 (t, $^2J_{CF}=21.9$ Hz; CH_2CF_2,), 68.0 (CH_2O), 114.7, 115.7 (tt, $^1J_{CF}=297.6$ Hz, $^2J_{CF}=35.4$ Hz; CF_2), 117.1 (tt, $^1J_{CF}=254.6$ Hz, $^2J_{CF}=26.1$ Hz; CF_2), 126.6, 127.5, 127.9, 129.7, 130.1, 130.7, 131.2, 132.6, 140.5, 147.6, 158.8 ppm; HRMS (ESI): *m*/*z* calcd for $C_{32}H_{38}F_4NaO_3S^+$: 601.2370 $[M+Na^+]$; found: 601.2351.

(3-(4′-Butoxybiphenyl-4-yl)-1,1,2-trifluoroallyl)(*p*-tolyl)sulfane (25a): Obtained as a mixture of *Z*/*E* isomers 96:4; white solid, yield 84%, $R_f=0.4$ (hexane/$CH_2Cl_2=8:1$); m.p. 137.3–138.8 °C; *Z* isomer: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=1.03$ (t, $J=7.3$ Hz, 3H; CH_3), 1.55 (quin, $J=7.5$ Hz, 2H; CH_2), 1.83 (quin, $J=7.0$ Hz, 2H; CH_2), 2.39 (s, 3H; CH_3), 4.04 (t, $J=6.6$ Hz, 2H; CH_2O), 6.07 (d, $J_{HF}=36.1$ Hz, 1H; CH=CF), 7.01 (d, $J=8.6$ Hz, 2H; Ar), 7.20 (d, $J=7.8$ Hz, 2H; Ar), 7.51–7.60 ppm (m, 8H; Ar); ^{19}F NMR (377 MHz, $CDCl_3$): $\delta=-79.8$ (d, $J=19.8$ Hz; CF_2-S), −123.5 ppm (dt, $J_{HF}=36.1$ Hz, $J=19.8$ Hz; CF=CH); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=13.8$, 19.2, 21.2, 31.3, 67.7 (CH_2O), 110.1 (s), 114.8, 122.5, 122.8 (td, CF_2-CF, $^1J_{CF}=276.5$ Hz, $^2J_{CF}=38.8$ Hz), 126.9, 127.9, 128.9, 129.8 (d, $^4J_{CF}=6.8$ Hz), 130.0, 132.4, 136.7, 140.8, 141.2, 148.8 (dt, $^1J_{CF}=266.4$ Hz, $^2J_{CF}=31.2$ Hz; CF-CF_2,), 159.1 ppm; *E* isomer: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=6.65$ ppm (d, $J=23.0$ Hz, 1H; CH=CF,); the other signals are identical to those of the *Z*-isomer; IR (neat): $\tilde{\nu}=1470$, 1600 (Ar), 1680 cm^{-1} (C=C); HRMS (ESI): *m*/*z* calcd for $C_{26}H_{25}F_3NaOS^+$: 465.1470 $[M+Na^+]$; found: 465.1470.

***p*-Tolyl(1,1,2-trifluoro-3-(4′-(hexyloxy)biphenyl-4-yl)allyl)sulfane (25b)**: Obtained as a mixture of *Z*/*E* isomers (91:9); white solid, yield 82%; $R_f=0.5$ (hexane/$CH_2Cl_2=8:1$); *Z* isomer: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=0.96$ (t, $J=6.19$ Hz, 3H; CH_3), 1.35–1.42 (m, 4H; CH_2), 1.52 (quin, $J=7.3$ Hz, 2H; CH_2), 1.85 (quin, $J=7.1$ Hz, 2H; CH_2), 2.39 (s, 3H; CH_3), 4.03 (t, $J=6.6$ Hz, 2H; CH_2O), 6.1 (d, $J_{HF}=36.4$ Hz, 1H; CH=CF,), 7.01 (d, $J=8.6$ Hz, 2H; Ar), 7.21 (d, $J=7.6$ Hz, 2H; Ar), 7.51–7.60 ppm (m, 8H; Ar); ^{19}F NMR (377 MHz, $CDCl_3$): $\delta=-79.9$ (d, $J=19.8$ Hz; CF_2-S), −123.6 ppm (dt, $J_{H\text{-}F}=36.4$ Hz, $J=19.8$ Hz; CF=CH); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=14.0$, 21.2, 22.6, 25.7, 29.2, 31.6, 68.0 (CH_2O), 110.1, 114.8, 122.5, 122.9 (td, $^1J_{CF}=277.4$ Hz, $^2J_{CF}=38.8$ Hz; CF_2-CF), 126.6, 127.9, 128.9, 129.8 (d, $^4J_{CF}=7.3$ Hz), 130.0, 132.3, 136.7, 140.7, 141.2, 148.8 (dt, $^1J_{CF}=267.1$ Hz, $^2J_{CF}=31.5$ Hz; CF-CF_2,), 159.1 ppm; *E* isomer: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=6.65$ ppm (d, $J=22.5$ Hz, 1H; CH=CF,); the other signals are identical to those of the *Z* isomer; IR (neat): $\tilde{\nu}=1470$, 1610 (Ar), 1680 cm^{-1} (C=C); HRMS (ESI): *m*/*z* calcd for $C_{28}H_{29}F_3NaOS^+$: 493.1783 $[M+Na^+]$; found: 493.1783.

(3-(4′-(Decyloxy)biphenyl-4-yl)-1,1,2-trifluoroallyl)(*p*-tolyl)sulfane (25c): obtained as a mixture of *Z*/*E* isomers (99:1); white solid, yield 85%; $R_f=0.5$ (hexane/$CH_2Cl_2=8:1$); *Z* isomer: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=0.93$ (t, $J=5.8$ Hz, 3H; CH_3), 1.25–1.56 (m, 14H; CH_2), 1.85 (quin, $J=6.9$ Hz, 2H; CH_2), 2.39 (s, 3H; CH_3), 4.03 (t, $J=6.4$ Hz, 2H; CH_2O), 6.08 (d, $J_{HF}=36.4$ Hz, 1H; CH=CF), 7.01 (d, $J=8.6$ Hz, 2H; Ar), 7.21 (d, $J=7.8$ Hz, 2H; Ar), 7.51–7.60 ppm (m, 8H; Ar); ^{19}F NMR (377 MHz, $CDCl_3$): $\delta=-79.9$ (d, $J=19.9$ Hz; CF_2-S), −123.6 ppm (dt, $J_{HF}=36.4$ Hz, $J=19.9$ Hz; CF=CH); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=14.1$, 21.2, 22.7, 26.1, 29.3, 29.4, 29.4, 29.6, 29.7, 31.9, 68.1 (CH_2O), 110.1, 114.8, 122.6, 122.9 (td, $^1J_{CF}=279.1$ Hz, $^2J_{CF}=37.9$ Hz; CF_2-CF,), 126.7, 127.9, 128.9, 129.8 (d, $^4J_{CF}=7.6$ Hz), 129.9, 132.4, 136.7, 140.7, 141.2, 148.9 (dt, $^1J_{CF}=267.3$ Hz, $^2J_{CF}=32.0$ Hz; CF-CF_2), 159.1 ppm; *E* isomer: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=6.65$ ppm (d, $J=22.2$ Hz, 1H; CH=CF); the other signals are identical to those of the *Z* isomer; IR (neat): $\tilde{\nu}=1470$, 1600 (Ar), 1680 cm^{-1} (C=C);HRMS (ESI): *m*/*z* calcd for $C_{32}H_{37}F_3NaOS^+$: 549.2409 $[M+Na^+]$; found: 549.2415.

***p*-Tolyl(1,1,2-trifluoro-3-(4′-(pentadecyloxy)biphenyl-4-yl)allyl)sulfane (25d)**: obtained as a mixture of *Z*/*E* isomers (97:3); white solid, yield 76%, $R_f=0.2$ (hexane/$CH_2Cl_2=8:1$); m.p. 97.4–98.7 °C; *Z* isomer: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=0.91$ (t, $J=6.4$ Hz, 3H; CH_3), 1.24–1.43 (m, 22H; CH_2), 1.50 (quin, $J=7.2$ Hz, 2H; CH_2), 1.83 (quin, $J=6.9$ Hz, 2H; CH_2), 2.38 (s, 3H; CH_3), 4.03 (t, $J=6.4$ Hz. 2H; CH_2O), 6.07 (d, $J_{HF}=36.1$ Hz, 1H; CH=CF), 7.00 (d, $J=8.6$ Hz, 2H; Ar), 7.20 (d, $J=7.8$ Hz, 2H; Ar), 7.51–7.60 ppm (m, 8H; Ar); ^{19}F NMR (188 MHz, $CDCl_3$): $\delta=-80.4$ (d, $J=20.0$ Hz; CF_2-S), −124.1 ppm (dt, $J_{HF}=36.1$ Hz, $J=20.0$ Hz; CF=CH); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=14.1$, 21.2, 22.7, 26.1, 29.3, 29.4, 29.6- 29.9 (m, 8 CH_2), 31.9, 68.0 (CH_2O), 110.1, 119.8, 122.5, 122.9 (td, $^1J_{CF}=277.4$ Hz, $^2J_{CF}=38.8$ Hz; CF_2-CF), 126.6, 127.9, 128.9, 129.8 (d, $^4J_{CF}=6.8$ Hz), 129.9, 132.3, 136.7, 140.7, 141.2, 148.8 (dt, $^1J_{CF}=266.4$ Hz, $^2J_{CF}=29.5$ Hz; CF-CF_2), 159.1 ppm; *E* isomer: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=6.64$ ppm (d, $J=22.0$ Hz, 1H; CH=CF); the other signals are identical to those of the *Z* isomer; IR (neat): $\tilde{\nu}=1460$, 1600 (Ar), 1680 cm^{-1} (C=C); HRMS (ESI): *m*/*z* calcd for $C_{37}H_{47}F_3NaOS^+$: 619.3192 $[M+Na^+]$; found: 619.3193.

***p*-Tolyl(1,1,2-trifluoro-3-(4′-(octadecyloxy)biphenyl-4-yl)allyl)sulfane (25e)**: Obtained as a mixture of *Z*/*E* isomers (94:6); white solid, yield 71%; $R_f=0.2$ (hexane/$CH_2Cl_2=8:1$); *Z* isomer: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=0.91$ (t, $J=6.7$ Hz, 3H; CH_3), 1.24–1.43 (m, 28H; CH_2), 1.50 (quin, $J=7.4$ Hz, 2H; CH_2), 1.83 (quin, $J=7.1$ Hz, 2H; CH_2), 2.38 (s, 3H; CH_3), 4.03 (t, $J=6.6$ Hz, 2H; CH_2O), 6.07 (d, $J_{HF}=36.1$ Hz, 1H; CH=CF), 7.00 (d, $J=8.6$ Hz, 2H; Ar), 7.20 (d, $J=7.8$ Hz, 2H; Ar), 7.52–7.59 ppm (m, 8H; Ar); ^{19}F NMR (188 MHz, $CDCl_3$): $\delta=-80.4$ (d, $J=20.2$ Hz; CF_2-S), −124.11 ppm (dt, $J_{HF}=36.1$ Hz, $J=20.2$ Hz; CF=CH); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=14.1$, 21.3, 22.7, 26.1, 29.3, 29.4, 29.5, 29.6–29.8 (m, 10 CH_2), 32.0, 68.1 (CH_2O), 110.1, 114.9, 122.6, 122.9 (td, $^1J_{CF}=277.4$ Hz, $^2J_{CF}=37.9$ Hz; CF_2-CF), 126.7, 128.0, 129.0, 129.8 (d, $^4J_{CF}=7.6$ Hz), 130.0, 132.4, 136.7, 140.8, 141.2, 148.9 (dt, $^1J_{CF}=265.6$ Hz, $^2J_{CF}=30.4$ Hz; CF-CF_2), 159.1 ppm; *E* isomer: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=6.64$ ppm (d, $J=22.5$ Hz, 1H; CH=CF); the other signals are identical to those of the Z isomer; IR (neat): $\tilde{\nu}=1460$, 1600 (Ar), 1680 cm^{-1} (C=C); HRMS (ESI): *m*/*z* calcd for $C_{40}H_{53}F_3NaOS^+$: 661.3661 $[M+Na^+]$; found: 661.3683.

(*Z*)-4-Butoxy-4′-(2,3,3-trifluoro-3-tosylprop-1-enyl)biphenyl (26a): White solid, yield 85%, $R_f=0.3$ (hexane/$CH_2Cl_2=2:1$); m.p. 149.9–150.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=1.02$ (t, $J=7.5$ Hz, 3H; CH_3), 1.54 (quin, $J=7.2$ Hz, 2H; CH_2), 1.82 (quin, $J=6.9$ Hz, 2H; CH_2), 2.53 (s, 3H; CH_3), 4.04 (t, $J=6.4$ Hz, 2H; CH_2O), 6.44 (d, $J_{HF}=36.1$ Hz, 1H; CH=CF), 7.01 (d, $J=8.6$ Hz, 2H; Ar), 7.46 (d, $J=8.1$ Hz, 2H; Ar), 7.57 (d, $J=8.6$ Hz, 2H; Ar), 7.62 (d, $J=8.3$ Hz, 2H; Ar), 7.65 (d, $J=8.6$ Hz, 2H; Ar), 7.95 ppm (d, $J=8.1$ Hz, 2H; Ar); ^{19}F NMR (188 MHz, $CDCl_3$): $\delta=-108.2$ (d, $J=15.9$ Hz; CF_2-SO_2), −126.1 ppm (dt, $J_{H\text{-}F}=36.1$ Hz, $J=15.9$ Hz; CF=CH); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=13.8$, 19.2, 21.8, 31.2, 67.7 (CH_2O), 114.8, 115.6, 116.7 (td, $^1J_{CF}=288.3$ Hz, $^2J_{CF}=35.4$ Hz; CF_2-CF), 126.7, 128.0, 128.2, 129.2, 130.1, 130.3 (d, $^4J_{CF}=7.6$ Hz), 130.8, 132.1, 142.0, 144.1 (dt, $^1J_{CF}=268.9$ Hz, $^2J_{CF}=27.0$ Hz; CF-CF_2), 147.3, 159.2 ppm; IR (neat): $\tilde{\nu}=1360$, 1470, 1600 (Ar), 1680 cm^{-1} (C=C); HRMS (ESI): *m*/*z* calcd for $C_{26}H_{25}F_3NaO_3S^+$: 497.1369 $[M+Na^+]$; found: 497.1371.

(*Z*)-4-(Hexyloxy)-4′-(2,3,3-trifluoro-3-tosylprop-1-enyl)biphenyl (26b): White solid, yield 81%, $R_f=0.3$ (hexane/$CH_2Cl_2=2:1$); m.p. 141.2–142.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=0.93$ (t, 3H, CH_3, $J=7.07$ Hz), 1.34–1.42 (m, 4H, CH_2), 1.50 (quin, $J=7.1$ Hz, 2H, CH_2), 1.83 (quin, $J=7.0$ Hz, 2H, CH_2), 2.53 (s, 3H, CH_3), 4.03 (t, 2H, CH_2O, $J=6.6$ Hz), 6.44 (d, 1H, CH=CF, $J_{HF}=35.9$ Hz), 7.01 (d, 2H, Ar, $J=8.8$ Hz), 7.46 (d, 2H, Ar, $J=8.1$ Hz), 7.57 (d, 2H, Ar, $J=8.6$ Hz), 7.61 (d, 2H, Ar, $J=8.6$ Hz), 7.65 (d, 2H, Ar, $J=8.3$ Hz), 7.95 ppm (d, 2H, Ar, $J=8.1$ Hz); ^{19}F NMR (188 MHz, $CDCl_3$): $\delta=-108.2$ (d, $J=15.9$ Hz; CF_2-SO_2), −126.1 ppm (dt, $J_{H\text{-}F}=35.9$ Hz, $J=15.9$ Hz; CF=CH); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=14.0$, 21.8, 22.6, 25.7, 29.2, 31.5, 68.1 (CH_2O), 114.9, 115.6, 116.7 (td, $^1J_{CF}=287.5$ Hz, $^2J_{CF}=34.6$ Hz; CF_2-CF), 126.8, 128.0, 128.3, 129.4, 130.1, 130.3 (d, $^4J_{CF}=7.6$ Hz), 130.8, 132.1, 142.0, 144.1 (dt, $^1J_{CF}=269.1$ Hz, $^2J_{CF}=26.2$ Hz; CF-CF_2), 147.2, 159.2 ppm; IR (neat): $\tilde{\nu}=1370$, 1470, 1600 (Ar), 1680 cm^{-1} (C=C); elemental analysis calcd (%) for $C_{28}H_{29}F_3O_3S$: C 67.58, H 6.03; found: C 66.91, H 5.82.

(*Z*)-4-(Decyloxy)-4′-(2,3,3-trifluoro-3-tosylprop-1-enyl)biphenyl (26c): White solid, yield 81%, $R_f=0.4$ (hexane/$CH_2Cl_2=2:1$); m.p. 124.2–125.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=0.91$ (t, $J=6.82$ Hz, 3H; CH_3), 1.25–1.44 (m, 12H; CH_2), 1.51 (quin, $J=7.1$ Hz, 2H; CH_2), 1.83 (quin, $J=6.9$ Hz, 2H; CH_2), 2.53 (s, 3H; CH_3), 4.03 (t, $J=6.6$ Hz, 2H; CH_2O), 6.44 (d, $J_{HF}=36.0$ Hz, 1H; CH=CF), 7.00 (d, $J=8.8$ Hz, 2H; Ar), 7.47 (d, $J=8.0$ Hz, 2H; Ar), 7.57 (d, $J=8.6$ Hz, 2H; Ar), 7.62 (d, $J=8.6$ Hz, 2H; Ar), 7.65 (d, $J=8.6$ Hz, 2H; Ar), 7.95 ppm (d, $J=8.1$ Hz, 2H; Ar); ^{19}F NMR (188 MHz, $CDCl_3$): $\delta=-108.2$ (d, $J=15.9$ Hz; CF_2-SO_2), −126.1 ppm (dt, $J_{HF}=36.0$ Hz, $J=15.9$ Hz; CF=CH); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=14.1$, 21.8, 22.6, 26.0, 29.2, 29.3, 29.4, 29.5, 29.7 (m, 5*C*H$_2$), 31.9, 68.0 (*C*H$_2$O), 114.8, 115.6, 116.7 (td, $^1J_{\text{CF}}=288.3$ Hz, $^2J_{\text{CF}}=34.5$ Hz; *C*F$_2$-CF), 126.7, 128.0, 128.3, 129.3, 130.1, 130.3 (d, $^4J_{\text{CF}}=6.8$ Hz), 130.8, 132.1, 142.0, 144.1 (dt, $^1J_{\text{CF}}=269.8$ Hz, $^2J_{\text{CF}}=27.0$ Hz; *C*F-CF$_2$), 147.3, 159.2 ppm; IR (neat): $\tilde{\nu}=1360$, 1470, 1600 (Ar), 1680 cm^{-1} (C=C); HRMS (ESI): *m*/*z* calcd for $C_{32}H_{37}F_3NaO_3S^+$: 581.2308 [*M*+Na$^+$]; found: 581.2288.

Synthesis of alkynes 27 and 28 by dehydrofluorination (general procedure): A solution of the corresponding alkane **17** or alkene **9** (1 mmol) in dry THF (10 mL) was cooled down to −80 °C in argon flow. Then, a solution of sodium hexamethyldisilazide (1 M) in THF (3 mL in case of alkane and 2 mL in case of alkene) was added dropwise at −80 °C within 2–3 h at stirring. After that, reaction mixture was allowed to warm to room temperature during 1 h. The solvent was evaporated and the residue was quenched with 1 M solution of HCl in water. The aqueous phase was extracted with CH_2Cl_2 (3×30 mL), the combined organic layers were washed with water (3×30 mL) and dried over $CaCl_2$. Evaporation of the solvent left a crude product that was purified by column chromatography on silica gel (eluent hexane/CH_2Cl_2=8:1).

(3-(4′-Butoxybiphenyl-4-yl)-1,1-difluoroprop-2-ynyl)(*p*-tolyl)sulfane (27 a): The product was purified by column chromatography (eluent hexane/CH_2Cl_2=8:1); white solid, yield 85 %, $R_f=0.2$ (hexane/CH_2Cl_2=8:1); m.p. 117.1–118.6 °C; ^{1}H NMR (400 MHz, CDCl$_3$): $\delta=1.03$ (t, $J=7.2$ Hz, 3 H; CH$_3$), 1.55 (quin, $J=7.0$ Hz, 2 H; CH$_2$), 1.82 (quin, $J=6.8$ Hz, 2 H; CH$_2$), 2.42 (s, 3 H; CH$_3$), 4.04 (t, $J=6.4$ Hz, 2 H; CH$_2$O), 7.00 (d, $J=8.6$ Hz, 2 H; Ar), 7.25 (d, $J=7.8$ Hz, 2 H; Ar), 7.48 (d, $J=8.1$ Hz, 2 H; Ar), 7.52–7.58 (m, 4 H; Ar), 7.61 ppm (d, $J=7.8$ Hz, 2 H; Ar); ^{19}F NMR (188 MHz, CDCl$_3$): $\delta=-59.1$ ppm (s; C*F*$_2$-S); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta=13.8$, 19.2, 21.2, 31.3, 67.7 (*C*H$_2$O), 80.6 (t, $^2J_{\text{CF}}=40.5$ Hz; C≡*C*-CF$_2$), 90.5, 114.8, 117.4, 118.0 (t, $^1J_{\text{CF}}=264.7$ Hz; CF$_2$), 123.3, 126.4, 128.0, 129.9, 131.8, 132.5, 136.7, 140.8, 142.5, 159.3 ppm; IR (neat): $\tilde{\nu}=1120$, 1470, 1610 (Ar), 2250 cm^{-1} (C≡C); elemental analysis calcd (%) for $C_{26}H_{24}F_2OS$: C 73.50, H 5.85; found: C 73.91, H 5.73.

1,1-Difluoro-3-(4′-(hexyloxy)biphenyl-4-yl)prop-2-ynyl)(*p*-tolyl)sulfane (27 b): White solid, yield 83 %, $R_f=0.2$ (hexane/CH_2Cl_2=8:1); m.p. 96.6–97.9 °C; ^{1}H NMR (400 MHz, CDCl$_3$): $\delta=0.94$ (t, $J=7.0$ Hz, 3 H; CH$_3$), 1.35–1.42 (m, 4 H; CH$_2$),1.50 (quin, $J=7.3$ Hz, 2 H; CH$_2$), 1.83 (quin, $J=7.0$ Hz, 2 H; CH$_2$), 2.42 (s, 3 H; CH$_3$), 4.02 (t, $J=6.6$ Hz, 2 H; CH$_2$O), 7.00 (d, $J=8.6$ Hz, 2 H; Ar), 7.25 (d, $J=8.1$ Hz, 2 H; Ar), 7.48 (d, $J=8.1$ Hz, 2 H; Ar), 7.52–7.58 (m, 4 H; Ar), 7.61 ppm (d, $J=8.1$ Hz, 2 H; Ar); ^{19}F NMR (188 MHz, CDCl$_3$): $\delta=-59.2$ ppm (s; C*F*$_2$-S); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta=14.0$, 21.2, 22.6, 25.7, 29.2, 31.6, 68.0 (*C*H$_2$O), 80.6 (t, $^2J_{\text{CF}}=40.0$ Hz, C≡*C*-CF$_2$), 90.5, 114.9, 117.4, 118.0 (t, $^1J_{\text{CF}}=265.6$ Hz; CF$_2$), 123.4, 126.4, 128.0, 129.9, 131.8, 132.5, 136.7, 140.8, 142.5, 159.3 ppm; IR (neat): $\tilde{\nu}=1470$, 1600 (Ar), 2250 cm^{-1} (C≡C); HRMS (ESI): *m*/*z* calcd for $C_{28}H_{28}F_2NaOS^+$: 473.1721 [*M*+Na$^+$]; found: 473.1735.

(3-(4′-(Decyloxy)biphenyl-4-yl)-1,1-difluoroprop-2-ynyl)(*p*-tolyl)sulfane (27 c)*:* White solid, yield 85 %; $R_f=0.2$ (hexane/CH_2Cl_2=8:1); ^{1}H NMR (400 MHz, CDCl$_3$): $\delta=0.92$ (t, $J=6.7$ Hz, 3 H; CH$_3$), 1.30–1.42 (m, 8 H; CH$_2$), 1.50 (quin, $J=7.1$ Hz, 2 H; CH$_2$), 1.83 (quin, $J=7.0$ Hz, 2 H; CH$_2$), 2.42 (s, 3 H; CH$_3$), 4.02 (t, $J=6.6$ Hz, 2 H; CH$_2$O), 7.00 (d, $J=8.8$ Hz, 2 H; Ar), 7.25 (d, $J=7.8$ Hz, 2 H; Ar), 7.48 (d, $J=8.3$ Hz, 2 H; Ar), 7.52–7.58 (m, 4 H; Ar), 7.61 ppm (d, $J=7.8$ Hz, 2 H; Ar); ^{19}F NMR (188 MHz, CDCl$_3$): $\delta=-59.2$ ppm (s; C*F*$_2$-S); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta=14.1$, 21.3, 22.7, 26.0, 29.2, 29.3, 29.4, 29.5, 29.6, 31.9, 68.1 (*C*H$_2$O), 80.7 (t, $^2J_{\text{CF}}=40.0$ Hz; C≡*C*-CF$_2$), 90.5 (t, $^3J_{\text{CF}}=5.9$ Hz; *C*≡C-CF$_2$), 114.9, 117.5, 118.0 (t, $^1J_{\text{CF}}=265.6$ Hz; CF$_2$), 123.4, 126.4, 128.0, 129.9, 131.9, 132.5, 136.7, 140.8, 142.6, 159.3 ppm; IR (neat): $\tilde{\nu}=1470$, 1600 (Ar), 2250 cm^{-1} (C≡C); elemental analysis calcd (%) for $C_{32}H_{36}F_2OS$: C 75.58, H 7.18; found: C 75.85, H 7.16.

(1,1-Difluoro-3-(4′-(octadecyloxy)biphenyl-4-yl)prop-2-ynyl)(*p*-tolyl)sulfane (27 d): White solid, yield 91 %; $R_f=0.2$ (hexane/CH_2Cl_2=8:1); ^{1}H NMR (400 MHz, CDCl$_3$): $\delta=0.94$ (t, $J=6.6$ Hz, 3 H; CH$_3$), 1.28–1.42 (m, 16 H; CH$_2$), 1.47–1.56 (m, 2 H; CH$_2$), 1.80–1.90 (m, 2 H; CH$_2$), 2.43 (s, 3 H; CH$_3$), 4.04 (t, $J=5.8$ Hz, 2 H; CH$_2$O), 7.01 (d, $J=8.1$ Hz, 2 H; Ar), 7.27 (d, $J=7.6$ Hz, 2 H; Ar), 7.49 (d, $J=7.8$ Hz, 2 H; Ar), 7.52–7.59 (m, 4 H; Ar), 7.64 ppm (d, $J=7.3$ Hz, 2 H; Ar); ^{19}F NMR (188 MHz, CDCl$_3$): $\delta=-59.2$ ppm (s; C*F*$_2$-S); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta=14.1$, 21.3, 22.7, 26.0, 29.2, 29.4, 29.5, 29.6–29.8 (m, 10 *C*H$_2$), 31.9, 68.0 (*C*H$_2$O), 80.7 (t, $^2J_{\text{CF}}=40.3$ Hz; C≡*C*-CF$_2$), 90.4 (t, $^3J_{\text{CF}}=5.9$ Hz; *C*≡C-CF$_2$), 114.9, 117.5, 118.0 (t, $^1J_{\text{CF}}=265.7$ Hz; CF$_2$), 123.4, 126.4, 128.0, 129.9, 131.8, 132.5, 136.6, 140.7, 142.5, 159.3 ppm; IR (neat): $\tilde{\nu}=1470$, 1600 (Ar), 2250 cm^{-1} (C≡C); HRMS (ESI): *m*/*z* calcd for $C_{40}H_{52}F_2OSNa^+$: 641.3599 [*M*+Na+]; found: 619.3599.

4-(3,3-Difluoro-3-(*p*-tolyloxy)prop-1-ynyl)-4′-(hexyloxy)biphenyl (28 a): White solid, yield 93 %; $R_f=0.4$ (hexane/CH_2Cl_2=4:1); ^{1}H NMR (400 MHz, CDCl$_3$): $\delta=0.94$ (t, $J=6.3$ Hz, 3 H; CH$_3$), 1.34–1.41 (m, 4 H; CH$_2$), 1.51 (quin, $J=7.3$ Hz, 2 H; CH$_2$), 1.83 (quin, $J=7.0$ Hz, 2 H; CH$_2$), 2.38 (s, 3 H; CH$_3$), 4.02 (t, $J=6.6$ Hz, 2 H; CH$_2$O), 7.00 (d, $J=8.8$ Hz, 2 H; Ar), 7.19–7.21 (m, 4 H; Ar), 7.48–7.56 ppm (m, 6 H; Ar); ^{19}F NMR (188 MHz, CDCl$_3$): $\delta=-50.8$ ppm (s; C*F*$_2$-S); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta=14.0$, 20.8, 22.6, 25.7, 29.2, 31.6, 68.0 (*C*H$_2$O), 78.9 (t, $^2J_{\text{CF}}=52.3$ Hz; C≡*C*-CF$_2$), 86.4 (t, $^3J_{\text{CF}}=5.7$ Hz; *C*≡C-CF$_2$), 114.6 (t,$^1J_{\text{CF}}=243.5$ Hz; CF$_2$), 114.9, 117.2, 121.7, 126.5, 128.1, 129.9, 131.9, 132.6, 135.7, 142.7, 148.4, 159.4 ppm; IR (neat): $\tilde{\nu}=1480$, 1600 (Ar), 2250 cm^{-1} (C≡C); HRMS (ESI): *m*/*z* calcd for $C_{28}H_{28}F_2NaO_2{}^+$: 457.1950 [*M*+Na$^+$]; found: 457.1959.

4-(3,3-Difluoro-3-(m-tolyloxy)prop-1-ynyl)-4′-(hexyloxy)biphenyl (28 b): White solid, yield 88 %; $R_f=0.4$ (hexane/CH_2Cl_2=4:1); m.p. 45.3–48.2 °C; ^{1}H NMR (400 MHz, CDCl$_3$): $\delta=0.96$ (t, $J=7.1$ Hz, 3 H; CH$_3$), 1.36–1.43 (m, 4 H; CH$_2$), 1.47–1.55 (m, 2 H; CH$_2$), 1.84 (quin, $J=7.0$ Hz, 2 H; CH$_2$), 2.42 (s, 3 H; CH$_3$), 4.03 (t, $J=6.6$ Hz, 2 H; CH$_2$O), 7.01 (d, $J=8.6$ Hz, 2 H; Ar), 7.09–7.14 (m, 3 H; Ar), 7.30 (t, $J=7.6$ Hz, 1 H; Ar), 7.48–7.59 ppm (m, 6 H; Ar); ^{19}F NMR (188 MHz, CDCl$_3$): $\delta=-50.6$ ppm (s; C*F*$_2$-S); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta=14.0$, 21.3, 22.6, 25.7, 29.2, 31.6, 68.1 (*C*H$_2$O), 78.9 (t, $^2J_{\text{CF}}=52.3$ Hz; C≡*C*-CF$_2$), 86.5 (t, $^3J_{\text{CF}}=6.2$ Hz; *C*≡C-CF$_2$), 114.5 (t, $^1J_{\text{CF}}=243.7$ Hz; CF$_2$), 114.9, 117.3, 118.7, 122.4, 126.5, 128.1, 128.7, 129.1, 131.9, 132.6, 139.6, 142.7, 150.6, 159.4 ppm; IR (neat): $\tilde{\nu}=1470$, 1600 (Ar), 2250 cm^{-1} (C≡C); HRMS (ESI): *m*/*z* calcd for $C_{28}H_{28}F_2NaO_2{}^+$: 457.1950 [*M*+Na$^+$]; found: 457.1947.

4-(3,3-Difluoro-3-(*o*-tolyloxy)prop-1-ynyl)-4′-(hexyloxy)biphenyl (28 c): White solid, yield 95 %; $R_f=0.4$ (hexane/CH_2Cl_2=4:1); m.p. 43.5–45.6 °C; ^{1}H NMR (400 MHz, CDCl$_3$): $\delta=0.98$ (t, $J=6.6$ Hz, 3 H; CH$_3$), 1.37–1.45 (m, 4 H; CH$_2$), 1.53 (quin, $J=7.1$ Hz, 2 H; CH$_2$), 1.86 (quin, $J=7.0$ Hz, 2 H; CH$_2$), 2.43 (s, 3 H; CH$_3$), 4.04 (t, $J=6.6$ Hz, 2 H; CH$_2$O), 7.02 (d, $J=8.8$ Hz, 2 H; Ar), 7.18–7.32 (m, 3 H; Ar), 7.30 (t, $J=8.1$ Hz, 1 H; Ar,), 7.44–7.59 ppm (m, 6 H; Ar); ^{19}F NMR (188 MHz, CDCl$_3$): $\delta=-50.9$ ppm (s; C*F*$_2$-S); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta=14.0$, 22.6, 25.7, 29.2, 29.7, 31.6, 68.1 (*C*H$_2$O), 78.8 (t, $^2J_{\text{CF}}=52.7$ Hz; C≡*C*-CF$_2$), 86.3 (t, $^3J_{\text{CF}}=6.0$ Hz; *C*≡C-CF$_2$), 114.8 (t, $^1J_{\text{CF}}=236.3$ Hz; CF$_2$), 114.9, 117.2, 126.0, 126.5, 126.7, 128.1, 128.7, 131.2, 131.9, 132.6, 139.2, 142.7, 149.3, 159.4 ppm; IR (neat): $\tilde{\nu}=1470$, 1590 (Ar), 2250 cm^{-1} (C≡C); HRMS (ESI): *m*/*z* calcd for $C_{28}H_{28}F_2NaO_2{}^+$: 457.1950 [*M*+Na$^+$]; found: 457.1959.

4-(3-(4-*sec*-Butylphenoxy)-3,3-difluoroprop-1-ynyl)-4′-(hexyloxy)biphenyl (28 d): White solid, yield 91 %; $R_f=0.4$ (hexane/CH_2Cl_2=4:1); ^{1}H NMR (400 MHz, CDCl$_3$): $\delta=0.86$ (t, $J=7.3$ Hz, 3 H; CH$_3$), 0.95 (t, $J=7.1$ Hz, 3 H; CH$_3$,), 1.27 (d, $J=7.1$ Hz, 3 H; CH$_3$), 1.36–1.42 (m, 4 H, CH$_2$), 1.51 (quin, $J=7.1$ Hz, 2 H; CH$_2$), 1.63 (quin, $J=7.3$ Hz, 2 H; CH$_2$), 1.84 (quin, $J=7.1$ Hz, 2 H; CH$_2$), 2.65 (sex, $J=7.1$ Hz, 1 H; *CH*CH$_3$), 4.03 (t, $J=6.6$ Hz, 2 H; CH$_2$O), 7.00 (d, $J=8.6$ Hz; 2 H, Ar), 7.19–7.25 (m, 4 H, Ar), 7.48–7.56 ppm (m, 6 H, Ar); ^{19}F NMR (188 MHz, CDCl$_3$): $\delta=-50.68$ ppm (s, CF$_2$O); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta=12.2$, 14.0, 21.9, 22.6, 25.7, 29.2, 31.2, 31.6, 41.1, 68.1 (*C*H$_2$O), 78.93 (t, C≡*C*-CF$_2$, $^2J_{\text{CF}}=53.1$ Hz), 86.53 (t, *C*≡C-CF$_2$, $^3J_{\text{CF}}=5.7$ Hz), 114.9, 117.3 (t, CF$_2$,$^1J_{\text{CF}}=243.6$ Hz), 121.6, 126.5, 127.9, 127.9, 128.1, 132.0, 132.6, 142.7, 145.5, 148.6, 159.4 ppm; IR (neat): $\tilde{\nu}=1470$, 1590 (Ar), 2250 cm^{-1} (C≡C); HRMS (ESI-TOF): *m*/*z* calcd for $C_{31}H_{34}F_2NaO_2{}^+$ [*M*+Na$^+$]: 499.2419; found: 499.2424.

4-(3,3-Difluoro-3-(2-fluorophenoxy)prop-1-ynyl)-4′-(hexyloxy)biphenyl (28 e): white solid, yield 81 %; $R_f=0.4$ (hexane/CH_2Cl_2=4:1); m.p. 44.2–46.7 °C; ^{1}H NMR (400 MHz, CDCl$_3$): $\delta=0.95$ (t, $J=6.8$ Hz, 3 H; CH$_3$,), 1.35–1.43 (m, 4 H; CH$_2$), 1.51 (quin, $J=7.0$ Hz, 2 H; CH$_2$), 1.84 (quin, $J=7.0$ Hz, 2 H; CH$_2$), 4.03 (t, $J=6.4$ Hz, 2 H; CH$_2$O,), 7.00 (d, $J=8.8$ Hz, 2 H; Ar), 7.17 (t, $J=7.1$ Hz, 1 H; Ar), 7.21–7.27 (m, 2 H; Ar), 7.42 (t, $J=8.0$ Hz, 1 H; Ar), 7.49–7.58 ppm (m, 6 H; Ar); ^{19}F NMR (188 MHz, CDCl$_3$): $\delta=-51.7$ (s; C*F*$_2$-S), −128.9 ppm (m; ArF); ^{13}C NMR

(100 MHz, $CDCl_3$): $\delta = 14.1$, 22.61, 25.7, 29.7, 31.6, 68.2 (CH_2O), 79.0 (t, $^2J_{CF} = 52.3$ Hz; $C\equiv C$-CF_2), 86.6 (t, $^3J_{CF} = 6.2$ Hz; $C\equiv C$-CF_2), 114.1 (t, $^1J_{CF} = 245.4$ Hz; CF_2), 115.0, 117.1, 124.3, 125.9, 124.8, 126.6, 127.4, 128.2, 132.0, 132.7, 134.9, 138.0, 142.9, 159.4 ppm; IR (neat): $\tilde{\nu} = 1470$, 1600 (Ar), 2240 cm^{-1} ($C\equiv C$); HRMS (ESI): m/z calcd for $C_{27}H_{25}F_3NaO_2^+$: 461.1699 [$M+Na^+$]; found: 461.1710.

4-(3-(2-*tert*-Butylphenoxy)-3,3-difluoroprop-1-ynyl)-4′-(hexyloxy)biphenyl (28 f): White solid, yield 91 %; $R_f = 0.4$ (hexane/CH_2Cl_2 = 4:1); m.p. 42.1–44.6 °C; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 0.95$ (t, $J = 6.8$ Hz, 3H; CH_3), 1.36–1.42 (m, 4H; CH_2), 1.48 (s, 9H; *t*Bu), 1.48–1.53 (m, 2H; CH_2), 1.84 (quin, $J = 7.0$ Hz, 2H; CH_2), 4.02 (t, $J = 6.6$ Hz, 2H; CH_2O), 6.99 (d, $J = 8.6$ Hz, 2H; Ar), 7.19 (t, $J = 7.8$ Hz, 1H; Ar), 7.26 (t, $J = 7.8$ Hz, 1H; Ar), 7.40–7.47 (m, 2H; Ar), 7.49–7.65 ppm (m, 6H; Ar); ^{19}F NMR (188 MHz, $CDCl_3$): $\delta = -51.1$ ppm (s; CF_2-S); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 14.0$, 22.6, 25.7, 29.2, 29.7, 30.3, 31.6, 68.1 (CH_2O), 78.9 (t, $^2J_{CF} = 52.3$ Hz; $C\equiv C$-CF_2), 87.2 (t, $^3J_{CF} = 6.2$ Hz; $C\equiv C$-CF_2), 114.9, 115.1 (t, $^1J_{CF} = 240.8$ Hz; CF_2), 120.4, 125.1, 126.9, 127.2, 127.3, 128.1, 131.9, 132.5, 139.2, 141.0, 142.7, 150.5, 159.4 ppm; IR (neat): $\tilde{\nu} = 1470$, 1600 (Ar), 2250 cm^{-1} ($C\equiv C$); HRMS (ESI): m/z calcd for $C_{31}H_{34}F_2NaO_2^+$: 499.2419 [$M+Na^+$]; found: 499.2417.

Acknowledgements

Dr. A. V. Ryabchun, Dr. A. Y. Bobrovskiy, corresponding member of Russian academy of sciences, Dr. V. P. Shibaev are greatly acknowledged for measuring and interpretation of POM analysis. Dr. I. A.Uspenskaya, Dr. A. L. Emelina, Dr. M. A. Bykov are greatly acknowledged for the measurement of DSC. This research was supported by the Russian Foundation for Basic Research (grant no. 10-03-00897-a), Federal Special Program (grant P962) and Russian President Grant MK-7121.2012.3.

---

[1] a) P. Kirsch, *Modern Fluoroorganic Chemistry*, Weinheim, Wiley-VCH, **2004**, pp. 213–237; b) D. J. Byron, D. Lacey, R. C. Wilson, *Mol. Cryst. Liq. Cryst.* **1981**, *73*, 273–281; c) J. Dubois, A. Zann, A. Beguin, *Mol. Cryst. Liq. Cryst.* **1977**, *42*, 139–152; d) G. W. Gray, C. Hogg, D. Lacey, *Mol. Cryst. Liq. Cryst.* **1981**, *67*, 1–23; e) G. W. Gray, S. M. Kelly, *Mol. Cryst. Liq. Cryst.* **1981**, *75*, 109–119; f) P. Balkwill, D. Bishop, A. Pearson, I. Sage, *Mol. Cryst. Liq. Cryst.* **1985**, *123*, 1–13; g) J. E. Fearon, G. W. Gray, A. D. Fill, K. J. Toyne, *Mol. Cryst. Liq. Cryst.* **1985**, *124*, 89–103.

[2] a) P. Kirsch, M. Bremer, F. Huber, H. Lannert, A. Ruhl, M. Lieb, T. Wallmichrath, *J. Am. Chem. Soc.* **2001**, *123*, 5414–5417; b) E. Bartmann, *Adv. Mater.* **1996**, *8*, 570–573; c) P. Kirsch, M. Bremer, A. Taugerbeck, T. Wallmichrath, *Angew. Chem.* **2001**, *113*, 1528–1532; *Angew. Chem. Int. Ed.* **2001**, *40*, 1480–1484; d) Patent, Chisso Corporation, US6319570, **2001**; e) Patent, Chisso Corporation, US6001275, **1999**; f) Patent UBE INDUSTRIES, LTD., US2010/99909, **2010**; g) Patent, MERCK PATENT GMBH, WO2007/147516, **2007**; h) P. Kirsch, M. Lenges, A. Ruhl, D. V. Sevenard, G.-V. Roeschenthaler, *J. Fluorine Chem.* **2004**, *125*, 1025–1030.

[3] M. Hird, *Chem. Soc. Rev.* **2007**, *36*, 2070–2095.

[4] a) A. V. Shastin, V. N. Korotchenko, V. G. Nenajdenko, E. S. Balenkova, *Tetrahedron* **2000**, *56*, 6557–6563; b) V. N. Korotchenko, A. V. Shastin, V. G. Nenajdenko, E. S. Balenkova, *Synthesis* **2001**, 2081–2084; c) V. N. Korotchenko, A. V. Shastin, V. G. Nenajdenko, E. S. Balenkova, *J. Chem. Soc. Perkin Trans. 1* **2002**, 883–887; d) A. V. Shastin, V. G. Nenajdenko, V. N. Korotchenko, E. S. Balenkova, *Russ. Chem. Bull.* **2001**, *50*, 1401–1405; e) V. N. Korotchenko, V. G. Nenajdenko, A. V. Shastin, E. S. Balenkova, *Org. Biomol. Chem.* **2003**, *1*, 1906–1908; f) V. G. Nenajdenko, V. N. Korotchenko, A. V. Shastin, E. S. Balenkova, *Russ. Chem. Bull.* **2004**, *53*, 1034–1064; g) V. G. Nenajdenko, A. Y. Vasil′kov, A. A. Goldberg, V. M. Muzalevskiy, A. V. Naumkin, V. L. Podshibikhin, A. V. Shastin, E. S. Balenkova, *Mendeleev Commun.* **2010**, *20*, 200–202.

[5] a) V. G. Nenajdenko, A. V. Shastin, V. N. Korotchenko, G. N. Varseev, E. S. Balenkova, *Eur. J. Org. Chem.* **2003**, 302–308; b) V. N. Korotchenko, A. V. Shastin, V. G. Nenajdenko, E. S. Balenkova, *Tetrahedron* **2001**, *57*, 7519–7527; c) V. G. Nenajdenko, G. N. Varseev, V. N. Korotchenko, A. V. Shastin, E. S. Balenkova, *J. Fluorine Chem.* **2003**, *124*, 115–118; d) V. G. Nenajdenko, G. N. Varseev, V. N. Korotchenko, A. V. Shastin, E. S. Balenkova, *J. Fluorine Chem.* **2004**, *125*, 1339–1345; e) V. G. Nenajdenko, G. N. Varseev, A. V. Shastin, E. S. Balenkova, *J. Fluorine Chem.* **2005**, *126*, 907–913; f) A. V. Shastin, V. M. Muzalevsky, E. S. Balenkova, V. G. Nenajdenko, *Mendeleev Commun.* **2006**, *16*, 179–180; g) A. A. Goldberg, V. M. Muzalevskiy, A. V. Shastin, E. S. Balenkova, V. G. Nenajdenko, *J. Fluorine Chem.* **2010**, *131*, 384–388.

[6] M. Kozáková, M. Buděšínský, J. Hodačová, *Synth. Commun.* **2005**, *35*, 161–167.

[7] E. Pretsch, P. Bühlmann, M. Badertscher, *Structure Determination of Organic Compounds: Tables of Spectral Data*, Springer, Berlin, **2009**, p. 433.

[8] X. Y. Li, X. K. Jiang, H. Q. Pan, J. S. Hu, W. M. Fu, *Pure Appl. Chem.* **1987**, *59*, 1015–1020.

[9] Y. Pustovit, A. Alexeenko, S. Trofymchuk, O. Lukin, A. Tolmachev, *Synthesis* **2010**, 1159–1165.

[10] a) P. G. Gassman, N. J. O'Reilly, *Tetrahedron Lett.* **1985**, *26*, 5243–5246; b) P. G. Gassman, N. J. O'Reilly, *J. Org. Chem.* **1987**, *52*, 2481–2490.

[11] a) P. Johncock, *J. Organomet. Chem.* **1969**, *19*, 257–265; b) N. Y. Adonin, V. V. Bardin, U. Floerke, H. J. Fron, *Russ. J. Gen. Chem.* **2011**, *81*, 509–516; c) N. Y. Adonin, V. V. Bardin, H.-J. Frohn, *Z. Anorg. Allg. Chem.* **2007**, *633*, 647–652.

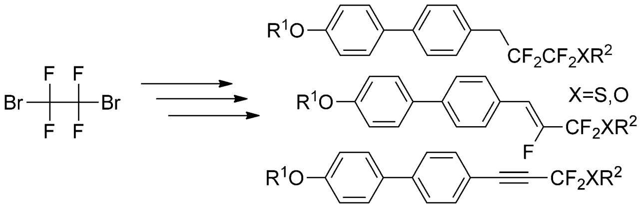
[12] a) V. M. Muzalevskiy, V. G. Nenajdenko, A. V. Shastin, E. S. Balenkova, G. Haufe, *Tetrahedron* **2009**, *65*, 6991–7000; b) V. G. Nenajdenko, V. M. Muzalevskiy, A. V. Shastin, E. S. Balenkova, E. V. Kondrashov, I. A. Ushakov, A. Y. Rulev, *J. Org. Chem.* **2010**, *75*, 5679–5688; c) A. Y. Rulev, V. M. Muzalevskiy, E. V. Kondrashov, I. A. Ushakov, A. V. Shastin, E. S. Balenkova, G. Haufe, V. G. Nenajdenko, *Eur. J. Org. Chem.* **2010**, 300–310.

[13] a) G. W. Gray, M. Hird, D. Lacey, K. J. Toyne, *J. Chem. Soc. Perkin Trans. 2* **1989**, 2041–2053; b) M. Kwiatkowski, J. Chattopadhyaya, *Acta Chem. Scand. Ser. B* **1984**, *38*, 657–671.

[14] a) C. M. Marson, L. D. Farrand, R. Brettle, D. A. Dunmur, *Tetrahedron* **2003**, *59*, 4377–4381; b) Z. N. Yu, H. L. Tu, X. H. Wan, X. F. Chen, Q. F. Zhou, *Mol. Cryst. Liq. Cryst.* **2003**, *391*, 41–56.

[15] I. Rico, C. Wakselman, *J. Fluorine Chem.* **1982**, *20*, 759.

Received: September 17, 2012



Clear as liquid crystal: A flexible three-step pathway to the new family of CF_2CF_2S-bridged alkanes, CF_2S-, CF_2O-bridged alkenes, and alkynes was elaborated, starting from 1,2-dibromoethane. Simplicity of the reaction procedures, high universality, and liquid crystalline characteristics of the compound are attractive features of the method proposed, which provides opportunities for the synthesis of new liquid crystals (see scheme).

Liquid Crystals

V. G. Nenajdenko, A. A. Goldberg, V. M. Muzalevskiy, E. S. Balenkova, A. V. Shastin* .... ▮▮▮–▮▮▮

Design and Synthesis of a New Family of Fluorinated Liquid Crystals