

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
12 April 2012 (12.04.2012)

PCT

(10) International Publication Number
WO 2012/045290 A1

(51) International Patent Classification:
C07C 381/00 (2006.01)

(21) International Application Number:
PCT/CZ2011/000097

(22) International Filing Date:
5 October 2011 (05.10.2011)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
PV 2010-729 7 October 2010 (07.10.2010) CZ

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(81) Designated States (unless otherwise indicated, for every
kind of national protection available): AE, AG, AL, AM,
AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ,
CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO,
DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT,
HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP,

KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD,
ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI,
NO, NZ, OM, PE, PG, PH, PL, PT, QA, RO, RS, RU,
RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ,
TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA,
ZM, ZW.

(84) Designated States (unless otherwise indicated, for every
kind of regional protection available): ARIPO (BW, GH,
GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ,
UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD,
RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ,
DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT,
LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS,
SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM,
GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

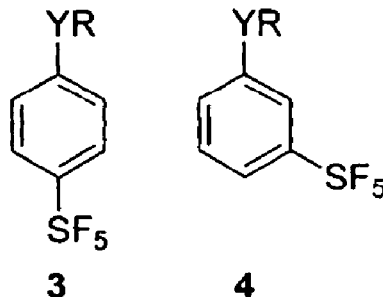
Declarations under Rule 4.17:

- as to the identity of the inventor (Rule 4.17(i))
- as to applicant's entitlement to apply for and be granted
a patent (Rule 4.17(ii))
- of inventorship (Rule 4.17(iv))

Published:

- with international search report (Art. 21(3))
- before the expiration of the time limit for amending the
claims and to be republished in the event of receipt of
amendments (Rule 48.2(h))

(54) Title: PROCESS FOR THE PREPARATION OF 3- AND 4-(PENTAFLUOROSULFANYL)BENZENES



(57) Abstract: Process for the preparation of substituted 3- and 4-(pentafluorosulfanyl)benzenes of general formula 3 and 4 by nucleophilic aromatic substitution, where nitrobenzene having pentafluorosulfanyl group connected in position 3 or 4 is allowed to react in concentration range 0.01 to 8.0 mol.l⁻¹ with compound RY·M⁺, where R is selected from a group comprising saturated, unsaturated, acyclic, cyclic or aromatic, substituted or unsubstituted carbon chain, Y is the element of VI. B group and M⁺ is the metal ion, in an organic solvent. The invention includes also further chemical modifications of primary products.

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Process for the preparation of 3- and 4-(pentafluorosulfanyl)benzenes

Field of the Invention

The invention is related to the preparation of substituted aromatic compounds containing the pentafluorosulfanyl (SF₅) functional group in position 3 or 4, by nucleophilic aromatic substitution of nitro-(pentafluorosulfanyl)benzenes.

Background Art

Organic compounds with pentafluorosulfanyl (SF₅) groups display a unique set of physicochemical properties. This includes extreme kinetic stability, strong electron acceptor capability, high lipophilicity and high SF₅ group electronegativity. A very high dipole moment can be achieved by the introduction of the SF₅ group to an organic molecule without increasing molecular polarity. Compounds with the SF₅ group are hydrolytically stable. For example, aromatic derivatives are unreactive towards strong Brønsted acids and bases. Thanks to these properties the pentafluorosulfanyl group was used in the design of new bioactive compounds and materials such as polymers and liquid crystals (Kirsch, P. *Modern Fluoroorganic Chemistry: Synthesis, Reactivity, and Applications*, Wiley-VCH, Weinheim, Germany, **2004**, pp. 146–156; Winter, R. W.; Dodean, R. A.; Gard, G. L. in *ACS Symposium Series, 911: Fluorine-Containing Synthons* (Soloshonok, V. A.; ed.), ACS Press, Washington, DC, **2005**, pp. 87–118; Kirsch, P.; Röschenhaler, G.-V. in *ACS Symposium Series, 949: Current Fluoroorganic Chemistry* (Soloshonok, V. A.; Mikami, K.; Yamazaki, T.; Welch, J. T.; Honek, J. F.; eds.), ACS Press, Washington, DC, **2007**, pp. 221–243; Crowley, P. J.; Mitchell, G.; Salmon, R.; Worthington, P. A. *Chimia* **2004**, *58*, 138). Further development of the use of compounds with the SF₅ group for various applications is hampered by a very limited number of commercially available chemicals containing this functional group and their high price.

Selective introduction of the pentafluorosulfanyl group into aliphatic compounds is usually achieved by radical addition of SF₅X (X = Cl, Br) to unsaturated compounds (Aït-Mohand, S.; Dolbier, Jr., W. D. *Org. Lett.* **2001**, *4*, 3013; Dolbier, Jr., W. D.; Aït-Mohand, S.; Schertz, T. D.; Sergeeva, T. A.; Cradlebaugh, J. A.; Mitani, A.; Gard, G. L.; Winter, R. W.; Thrasher, J. S. *J. Fluorine Chem.* **2006**, *127*, 1302); however access to SF₅Cl and SF₅Br is very difficult

(Jonethal, U.; Kuschel, R.; Seppelt, K. *J. Fluorine Chem.* **1998**, *88*, 3; Winter, R.; Terjeson, R. J.; Gard, G. L. *J. Fluorine Chem.* **1998**, *89*, 105; Tullock, C. W.; Coffman, D. D.; Muetterties, E. L. *J. Am. Chem. Soc.* **1964**, *86*, 357) and the chemistry of aliphatic SF₅ derivatives thus remains relatively unexplored.

Reaction of benzene with S₂F₁₀ or oxidative fluorination of diaryldisulfides with AgF₂ are known methods for the preparation of (pentafluorosulfanyl)benzenes; however they work only in very low yields and are not very reproducible (Roberts, H. L. *J. Chem. Soc.* **1962**, 3183; Sheppard, W. A. *J. Am. Chem. Soc.* **1960**, *82*, 4752; Sheppard, W. A. *J. Am. Chem. Soc.* **1962**, *84*, 3064).

In 1990s improved procedure for the preparation of (pentafluorosulfanyl)benzenes was developed which is based on fluorination of bis(nitrophenyl)disulfides using elemental fluorine-(Bowden, R. D.; Greenhall, M. P.; Moilliet, J. S.; Thomson, J. *US 5741935*, **1997** a *WO 9705106*, **1997**; Bowden, R. D.; Comina, P. J.; Greenhall, M. P.; Kariuki, B. M.; Loveday, A.; Philp, D. *Tetrahedron* **2000**, *56*, 3399).

This methodology, which was later improved by the use of a microreactor for elemental fluorine, provided access to larger quantities of 1-nitro-4-(pentafluorosulfanyl)benzene (**1**) and 1-nitro-3-(pentafluorosulfanyl)benzene (**2**) (Chambers, R. D.; Spink, R. C. H. *Chem. Commun.* **1999**, 883). This method requires the presence of nitro group substituted aromatic ring otherwise side products containing fluorine atoms on the aromatic ring are formed. In recent years, a two step method for the preparation of aromatic compounds containing the SF₅ group was developed and patented by Umemoto (Umemoto, T. *WO 2008/118787*, **2008**). In the first step, diaryldisulfides react with chlorine in the presence of potassium fluoride to give arylsulfurchlorotetrafluorides, which are then fluorinated in the second step using ZnF₂ or SbF₅ to pentafluorosulfanyl substituted aromatics.

Several synthetic transformations of aromatic compounds containing the SF₅ group are also described in literature. (Pentafluorosulfanyl)benzene undergoes nitration with concentrated nitric acid in the presence of sulfuric acid at 50 °C to give 1-nitro-3-(pentafluorosulfanyl)benzene (**2**) in 81% yield (Sheppard, W. A. *J. Am. Chem. Soc.* **1962**, *84*, 3064). 1-Nitro-4-(pentafluorosulfanyl)benzene (**1**) and 1-nitro-3-(pentafluorosulfanyl)benzene

(2) can be hydrogenated with hydrogen in the presence of catalyst in good yields to give the corresponding pentafluorosulfanyl anilines (Sheppard, W. A. *J. Am. Chem. Soc.* **1962**, *84*, 3064; Bowden, R. D.; Comina, P. J.; Greenhall, M. P.; Kariuki, B. M.; Loveday, A.; Philp, D. *Tetrahedron* **2000**, *56*, 3399; Kirsch, P.; Bremer, M.; Heckmeier, M.; Tarumi, K. *Angew. Chem. Int. Ed.* **1999**, *38*, 1989; Crowley, P. J.; Mitchell, G.; Salmon, R.; Worthington, P. A. *Chimia* **2004**, *58*, 138). These aniline derivatives could be further acylated to anilides, halogenated or diazotized. The diazonium salts undergo azo coupling, hydrolysis to substituted phenols, Sandmeyer reaction to yield the substituted halogenaromatics or reduction with H_3PO_2 . The published transformations of halo-(pentafluorosulfanyl)benzenes are: (a) lithiation using *t*-BuLi to give aryllithium compounds which can be further used for the introduction of hydroxyl or formyl functional groups, (b) formation of Grignard salts using MeMgI and follow-up reactions with electrophiles such as carbon dioxide, aldehydes or ketones, (c) palladium catalysed C-C cross-coupling reaction with phenylboronic acid (Suzuki coupling), phenyltributyltin (Stille coupling), phenylacetylene (Sonogashira coupling) or methyl acrylate (Heck coupling) (Sheppard, W. A. *J. Am. Chem. Soc.* **1962**, *84*, 3064; Bowden, R. D.; Comina, P. J.; Greenhall, M. P.; Kariuki, B. M.; Loveday, A.; Philp, D. *Tetrahedron* **2000**, *56*, 3399). Recently, it was found that the fluorine atom in 1-fluoro-4-nitro-2-(pentafluorosulfanyl)benzene and 1,3-dichloro-2-fluoro-5-(pentafluorosulfanyl)benzene can be substituted for various nucleophiles (Sipyagin, A. M.; Bateman, C. P.; Tan, Y.-T.; Thrasher, J. S. *J. Fluorine Chem.* **2001**, *112*, 287; Crowley, P. J.; Mitchell, G.; Salmon, R.; Worthington, P. A. *Chimia* **2004**, *58*, 138).

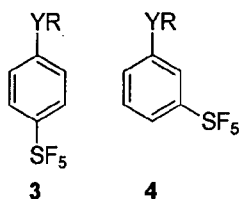
Aromatic nitro compounds are suitable for nucleophilic aromatic substitution due to the strong electron acceptor character of the nitro group (Ono, N. in *The Nitro Group in Organic Synthesis*, John Wiley & Sons, Inc., New York, **2001**, pp. 302–324; Beck, J. R. *Tetrahedron* **1978**, *34*, 3057). The nitro group is also a good leaving group and it can be often exchanged if the aromatic ring contains another electron acceptor groups such as NO_2 , CN, CO_2R or CF_3 . Nucleophilic aromatic substitution for nitro group in 1-nitro-4-(pentafluorosulfanyl)benzene (1) and 1-nitro-3-(pentafluorosulfanyl)benzene (2) has not been studied and our initial experiments in this direction were not successful. For example, the following reactions of 1-nitro-4-(pentafluorosulfanyl)benzene (1) with various nucleophiles did not provide products of substitution for the nitro group (although in a literature there are many examples of successful transformations that take place on substrates with an electron acceptor group

instead of SF₅ group): (a) reaction with excess NaOH or KOH in aqueous ethanol or dimethylformamide, or in the mixture of dichloromethane-water, in the presence or absence of phase transfer catalyst (C₁₆H₃₃NMe₃⁺Br⁻, Me = methyl) at 20–150 °C; (b) reaction with excess of PhSO₂Na (Ph=phenyl) in dimethylformamide at 20–100 °C; (c) reaction with excess of methyllithium or *n*-butyllithium or lithium salt of 2-nitropropane or lithium salt of aniline or lithium salt of morpholine or phenylmagnesiumchloride in tetrahydrofuran at low temperatures (0 °C to –78 °C); (d) reaction with excess of tetrabutylammoniumcyanide in dimethylsulfoxide at room temperature. Unsuccessful was also reaction of 1-nitro-4-(pentafluorosulfanyl)benzene (**1**) with excess of cesium fluoride in the presence of crown ether (15-crown-5) or with anhydrous tetrabutylammonium fluoride in dimethylsulfoxide at 20–80 °C, which gave a mixture of 1-fluoro-4-(pentafluorosulfanyl)benzene, 1-fluoro-4-nitrobenzene, nitrobenzene and (pentafluorosulfanyl)benzene, where the conversion of required 1-fluoro-4-(pentafluorosulfanyl)benzene was only 10–25 mol. %.

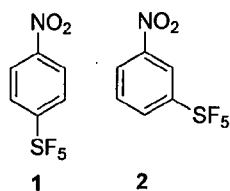
Due to the novelty of this theme and the above mentioned unsuccessful experiments, the discovery of smooth reactions of nitro-(pentafluorosulfanyl)benzenes with alcoholates and thiolates was completely surprising. Using these reactions, access to many derivatives of (pentafluorosulfanyl)benzene is now open by one step synthesis starting from commercial compounds. Subsequent chemical modifications of primary products allows the synthesis of additional new derivatives of (pentafluorosulfanyl)benzenes, or represents new and better way to known derivatives such as 3- and 4-(pentafluorosulfanyl)phenols.

Disclosure of the invention

The subject-matter of the invention is a process for the preparation of substituted 3- and 4-(pentafluorosulfanyl)benzenes of general formula **3** and/or **4**



by nucleophilic aromatic substitution characterized by reaction of nitrobenzene with pentafluorosulfanyl group connected in position 3 or 4 of general formula **1** and/or **2**,



in concentration range $0.01-8 \text{ mol.l}^{-1}$ with compounds RY^-M^+ , where R is chosen from a group containing saturated, unsaturated, acyclic, cyclic or aromatic, substituted or unsubstituted carbon chain, Y is the element of VI. B group and M^+ is the metal ion, in an organic solvent at temperatures ranging from $-55 \text{ }^\circ\text{C}$ or at least boiling point of the solvent to $150 \text{ }^\circ\text{C}$, giving the corresponding substituted compounds of general formula 3 and/or 4.

In one aspect of the method of the present invention the element Y is preferably chosen from the group comprising sulfur and oxygen for the preparation of substituted 4-(pentafluorosulfonyl)benzenes of general formula 3 and for the preparation of substituted 3-(pentafluorosulfonyl)benzenes of general formula 4 the element Y is preferably oxygen.

In another embodiment of the method of the present invention the metal ion M^+ is preferably chosen from the group comprising Na^+ , K^+ or organic cation, and better tetraalkylammonium.

In a preferred aspect of the method of the present invention, reactions are conducted in solvents chosen from the group comprising dimethylformamide, dimethylsulfoxide, dimethylacetamide and hexamethylphosphoramide.

In another preferred embodiment of the method of the present invention, reactions are conducted in the presence of excess of compound RY^-M^+ .

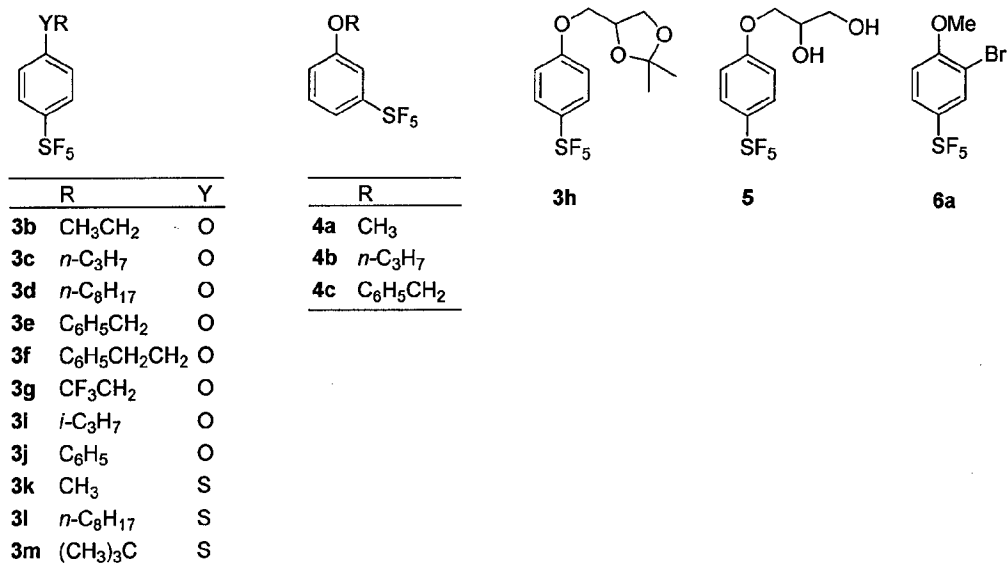
In a preferred embodiment the method of the present invention, reactions are conducted at room temperature in the concentration range of $0.1-4 \text{ mol.l}^{-1}$ of starting compound of formula 1 and/or 2.

An object of the present invention is the use of compounds of general formula 3 for the synthesis of 4-(pentafluorosulfonyl)phenol.

Another object of the present invention is also the use of compounds of general formula 4 for the synthesis of 3-(pentafluorosulfonyl)phenol.

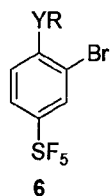
New compounds of following formulas are also the object of the present invention:

- 1-Ethoxy-4-(pentafluorosulfanyl)benzene of formula **3b**,
 1-(*n*-Propoxy)-4-(pentafluorosulfanyl)benzene of formula **3c**,
 1-(*n*-Octyloxy)-4-(pentafluorosulfanyl)benzene of formula **3d**,
 1-(Benzyloxy)-4-(pentafluorosulfanyl)benzene of formula **3e**,
 1-Phnethoxy-4-(pentafluorosulfanyl)benzene of formula **3f**,
 1-(Pentafluorosulfanyl)-4-(2,2,2-trifluoroethoxy)benzene of formula **3g**,
 2,2-Dimethyl-4-((4-(pentafluorosulfanyl)phenoxy)methyl)-1,3-dioxolane of formula **3h**,
 1-Isopropoxy-4-(pentafluorosulfanyl)benzene of formula **3i**,
 1-Phenoxy-4-(pentafluorosulfanyl)benzene of formula **3j**,
 Methyl(4-(pentafluorosulfanyl)phenyl)sulfide of formula **3k**,
n-Octyl(4-(pentafluorosulfanyl)phenyl)sulfide of formula **3l**,
t-Butyl(4-(pentafluorosulfanyl)phenyl)sulfide of formula **3m**,
 1-Methoxy-3-(pentafluorosulfanyl)benzene of formula **4a**,
 1-(*n*-Propoxy)-3-(pentafluorosulfanyl)benzene of formula **4b**,
 1-(Benzyloxy)-3-(pentafluorosulfanyl)benzene of formula **4c**,
 3-(4-(Pentafluorosulfanyl)phenoxy)propane-1,2-diol of formula **5**, and
 2-Bromo-1-methoxy-4-(pentafluorosulfanyl)benzene of formula **6a**



which can be used for the development of new biologically active compounds and materials.

Finally, the object of the present invention is also the use of compounds of general formula **3** for the synthesis of compounds of general formula **6**,



where compounds of general formula **3** react with brominating reagents in a suitable solvent to give compounds of general formula **6**.

Compounds RY^-M^+ , which are not commercially available were advantageously prepared *in situ* from compounds of formula RYH and a suitable base, which is for example sodium or potassium *tert*-butoxide. No detrimental effect of the formed *tert*-butanol on the outcome of the reaction was observed.

Reactions of compounds RY^-M^+ , which are derived from:

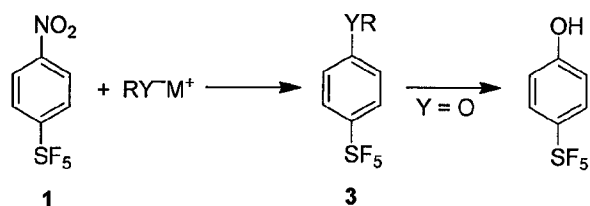
1. primary alcohols give products of general formula **3** in good yields (58–96 mol. %) in a short reaction time (0.3–3 hours);
2. secondary alcohols, aromatic alcohols and primary alkanethiols give products of general formula **3** in approximately 50 mol. % yields;
3. tertiary alcohols, pentafluorophenol and aromatic thiols do not give any products of general formula **3**, or only trace amounts of such products;
4. tertiary alkanethiols give low yields of products of general formula **3**;
5. primary alcohols give products of general formula **4** in approximately 50 mol. % yields;
6. aromatic alcohols and primary alkanethiols give only trace amounts of products of general formula **4**.

One of the products – 2,2-dimethyl-4-((4-(pentafluorosulfanyl)phenoxy)methyl)-1,3-dioxolane (**3h**) – was subjected to removal of the protecting ketal group using a literature method (Greene, T. W.; Wuts, P. G. M. in *Protective Groups in Organic Synthesis, Third Edition*, John Wiley & Sons, Inc., New York, 1999, pp. 211) to give 3-(4-(pentafluorosulfanyl)phenoxy)propane-1,2-diol (**5**) in 97 mol. % yield. This compound is structurally similar to commercially successful pharmaceutically used beta-blocker drugs such as chlorphenesin, chloranolol, propranolol, methocarbamol and others used as antiarrhythmic,

antihypertenzives, antianginal and antifungal agents. Because of structural similarity, comparable biological activity of newly obtained derivative can be expected, however results are not yet available.

Compounds of general formula **3**, where R is saturated, unsaturated, acyclic, cyclic or aromatic, substituted or unsubstituted carbon chain and Y is oxygen react further with reduction or nucleophilic reagents to give 4-(pentafluorosulfonyl)phenol according to Scheme 1.

In this reaction of compound of general formula **3**, where R is methyl and Y is oxygen, the excess of alkanethiol in dimethylformamide at elevated temperature was used in advantage according to literature (Kale, B.; Shinde, A.; Sonar, S.; Shingate, B.; Kumar, S.; Ghosh, S.; Venugopal, S.; Shingare, M. *Tetrahedron Lett.* **2010**, *51*, 3075).

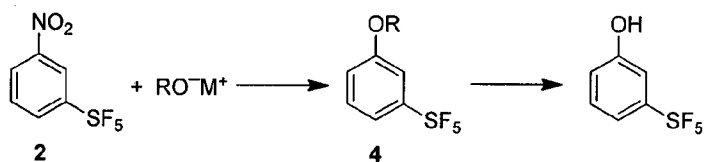


Scheme 1:

Preparation of substituted 4-(pentafluorosulfonyl)benzenes, compounds of general formula **3** from 1-nitro-4-(pentafluorosulfonyl)benzenecompound of formula **1** and preparation of 4-(pentafluorosulfonyl)phenol from compounds of general formula **3**.

Compounds of general formula **4**, where R is saturated, unsaturated, acyclic, cyclic or aromatic, substituted or unsubstituted carbon chain, react with reduction or nucleophilic reagents to give 3-(pentafluorosulfonyl)phenol according to Scheme 2.

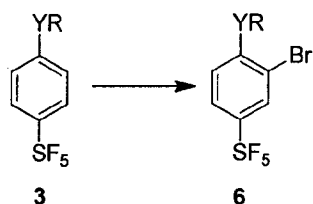
In such reaction, compounds of general formula **4**, where R is methyl, an excess of alkanethiol in dimethylformamide at elevated temperature was preferably used according to literature (Kale, B.; Shinde, A.; Sonar, S.; Shingate, B.; Kumar, S.; Ghosh, S.; Venugopal, S.; Shingare, M. *Tetrahedron Lett.* **2010**, *51*, 3075).



Scheme 2:

Preparation of substituted 3-(pentafluorosulfonyl)benzenes, compounds of general formula 4 from 1-nitro-3-(pentafluorosulfonyl)benzene, compound of formula 2 and preparation of 3-(pentafluorosulfonyl)phenol from compounds of general formula 4.

Compounds of general formula 3, where R is saturated, unsaturated, acyclic, cyclic, aromatic, substituted or unsubstituted carbon chain, Y is element of group VI. B, mainly oxygen and sulfur, react with bromination reagents in a suitable solvent to give compounds of general formula 6 according to Scheme 3. In this reaction, compounds of general formula 3 where R is methyl and Y is oxygen an excess of bromine in acetic acid at elevated temperature was advantageously used.



Scheme 3: Preparation of compounds of general formula 6 from compounds of general formula 3.

The above described preparations represent the best currently known preparations of compounds of general formula 3 and 4-(pentafluorosulfonyl)phenol according to Scheme 1, compounds of general formula 4 and 3-(pentafluorosulfonyl)phenol according to Scheme 2, and compounds of general formula 6 according to Scheme 3. Compounds of general formula 6 according to Scheme 3 could be used for further derivatization e.g. using a metal-catalyzed C–C cross-coupling reaction.

List of abbreviations

br s	broad signal
d	doublet
DMF	dimethylformamide

EI	electron impact ionization
eq.	equivalent(s)
Et	ethyl
IR	infrared spectroscopy
Me	methyl
mol.	Molar
Mp	melting point
MS	mass spectroscopy
NMR	nuclear magnetic rezonance
p	pentet
q	quartet
R_f	retention factor
t	triplet
<i>t</i> -Bu	tertiary butyl
THF	tetrahydrofuran

Examples

The subject-matter of present invention is supported by the following examples unless they limit the scope of the invention.

Example 1

1-Methoxy-4-(pentafluorosulfanyl)benzene (3a): Sodium methoxide (93 mg, 1.72 mmol, 1.5 eq.) was added to a stirred solution of 1-nitro-4-(pentafluorosulfanyl)benzene (**1**) (285 mg, 1.14 mmol) in DMF (1.14 mL) at room temperature. The resulting dark violet to black reaction mixture changed color to light brown within several minutes. After 30 minutes another portion of sodium methoxide (93 mg, 1.5 eq.) was added. After total reaction time of one hour, saturated aqueous solution of NH_4Cl (15 mL) and water (5 mL) were added and the product was extracted into *t*-BuOMe (3 × 20 mL). The combined organic phase was washed with saturated aqueous solution of NaCl (15 mL), dried with anhydrous MgSO_4 and the solvent was removed under reduced pressure. Column chromatography using silica gel (R_f 0.33, hexane) gave product **3a** as a colorless liquid (221 mg, 83 mol. %). IR (film, ν_{max} cm^{-1}) 3091, 3014, 2846, 1602, 1590, 1505, 1466, 1444, 1131, 1266, 1189, 1103, 1032, 841, 785, 585; ^1H NMR (400 MHz) 3.85 (s, 3H, OCH_3), 6.90–6.92 (m, 2H, $\text{C}_{\text{Ar}}\text{H}$), 7.67–7.70 (m, 2H,

$C_{Ar}H$); ^{19}F NMR (376 MHz) 63.8 (d, 4F, $^2J_{FF} = 150.0$ Hz, SF_4), 84.9–86.5 (m, 1F, SF); ^{13}C NMR (100 MHz) 55.6 (s, OCH_3), 113.5 (s, $C_{Ar}H$), 127.6 (p, $^3J_{CF} = 4.6$ Hz, $C_{Ar}H$), 146.7 (p, $^2J_{CF} = 17.6$ Hz, $C_{Ar}SF_5$), 161.4 (s, C_{Ar}); MS (EI) m/z 234 (M^+ , 100%), 215 (9), 126 (34), 111 (40), 107 (13), 92 (19), 83 (23), 77 (19), 63 (17); Calculated for $C_7H_7F_5OS$: C 35.90; H 3.01; F 40.56; S 13.69. Found: C 36.24; H 2.99; F 42.56; S 13.98.

Example 2

1-Ethoxy-4-(pentafluorosulfanyl)benzene (3b): Sodium ethanolate (68 mg, 1.5 mmol, 1.5 eq.) was added to a stirred solution of 1-nitro-4-(pentafluorosulfanyl)benzene (**1**) (249 mg, 1 mmol) in DMF (1 mL) at room temperature. After 30 minutes another portion of sodium ethanolate (68 mg, 1.5 eq.) was added. After total one hour reaction time, saturated aqueous solution of NH_4Cl (15 mL) and water (5 mL) were added and the product was extracted to *t*-BuOMe (3 × 20 mL). The combined organic phase was washed with saturated aqueous solution of NaCl (15 mL), dried with anhydrous $MgSO_4$ and solvent was removed under reduced pressure. Column chromatography using silica gel (R_f 0.32, hexane) gave product **3b** as a colorless liquid (184 mg, 74 mol. %). IR (film, ν_{max} cm^{-1}) 2988, 2935, 1600, 1588, 1506, 1265, 1189, 1102, 1046, 839; 1H NMR (400 MHz) 1.43 (t, 3H, $^3J_{HH} = 7.0$ Hz, CH_3), 4.07 (q, 2H, $^3J_{HH} = 7.0$ Hz, OCH_2), 6.88–6.90 (m, 2H, $C_{Ar}H$), 7.64–7.68 (m, 2H, $C_{Ar}H$); ^{19}F NMR (376 MHz) 63.8 (d, 4F, $^2J_{FF} = 150.0$ Hz, SF_4), 85.0–86.6 (m, 1F, SF); ^{13}C NMR (100 MHz) 14.6 (s, CH_3), 64.0 (s, OCH_2), 113.9 (s, $C_{Ar}H$), 127.6 (p, $^3J_{CF} = 4.6$ Hz, $C_{Ar}H$), 146.2–147.1 (m, $C_{Ar}SF_5$), 160.8 (s, C_{Ar}); MS (EI) m/z 248 (M^+ , 90%), 229 (13), 220 (82), 121 (10), 112 (100), 83 (15), 65 (18); Calculated for $C_8H_9F_5OS$: C 38.71; H 3.65; S 12.92. Found: C 38.91; H 3.81; S 13.04.

Example 3

1-(*n*-Propoxy)-4-(pentafluorosulfanyl)benzene (3c): Dry 1-propanol (214 μ L, 3.09 mmol) was added to a stirred solution of *t*-BuOK (347 mg, 3.09 mmol) in DMF (1.3 mL). Half of the resulting mixture was added dropwise to a stirred solution of 1-nitro-4-(pentafluorosulfanyl)benzene (**1**) (257 mg, 1.03 mmol) in DMF (0.5 mL). After ten minutes of stirring at room temperature the second half of the alkoxide mixture was added dropwise. After total 30 minutes reaction time, saturated aqueous solution of NH_4Cl (15 mL) and water (5 mL) were added and the product was extracted to Et_2O (3 × 20 mL). The combined organic phase was washed with saturated aqueous solution of NaCl (15 mL), dried with anhydrous

MgSO₄ and solvent was removed under reduced pressure. Column chromatography using silica gel (*R_f* 0.30, hexane) gave product **3c** as a colorless liquid (193 mg, 71 mol. %). IR (film, ν_{\max} cm⁻¹) 3089, 2972, 2943, 2883, 1601, 1587, 1505, 1265, 1188, 1102, 846, 818; ¹H NMR (400 MHz) 1.04 (t, 3H, ³*J*_{HH} = 7.4 Hz, CH₃), 1.77–1.87 (m, 2H, CH₂), 3.95 (t, 2H, ³*J*_{HH} = 6.5 Hz, OCH₂), 6.87–6.90 (m, 2H, C_{Ar}H), 7.64–7.67 (m, 2H, C_{Ar}H); ¹⁹F NMR (376 MHz) 63.8 (d, 4F, ²*J*_{FF} = 150.0 Hz, SF₄), 85.1–86.7 (m, 1F, SF); ¹³C NMR (100 MHz) 10.4 (s, CH₃), 22.4 (s, CH₂), 69.9 (s, OCH₂), 114.0 (s, C_{Ar}H), 127.6 (p, ³*J*_{CF} = 4.6 Hz, C_{Ar}H), 146.5 (p, ²*J*_{CF} = 17.5 Hz, C_{Ar}SF₅), 161.0 (s, C_{Ar}); MS (EI) *m/z* 262 (M⁺, 46%), 220 (100), 112 (50), 43 (23); Calculated for C₉H₁₁F₅OS: C 41.22; H 4.23; S 12.23. Found: C 41.49; H 4.29; S 12.30.

Example 4

1-(*n*-Octyloxy)-4-(pentafluorosulfanyl)benzene (3d): Dry *n*-octanol (1.29 ml, 8.17 mmol) was added to a stirred solution of *t*-BuOK (916 mg, 8.17 mmol) in DMF (5 mL). White suspension resulted after few minutes of stirring at room temperature. Solution of 1-nitro-4-(pentafluorosulfanyl)benzene (**1**) (509 mg, 2.04 mmol) in DMF (2 mL) was added and the resulting mixture was stirred for 20 minutes at room temperature. Saturated aqueous solution of NH₄Cl (15 mL) and water (5 mL) were added and the product was extracted to Et₂O (3 × 20 mL). The combined organic phase was washed with water (20 mL), saturated aqueous solution of NaCl (15 mL), dried with anhydrous MgSO₄ and solvent was removed under reduced pressure. Column chromatography using silica gel (*R_f* 0.46, hexane) gave product **3d** as a colorless liquid (564 mg, 83 mol. %). IR (film, ν_{\max} cm⁻¹) 3115, 3053, 2955, 2930, 2873, 2858, 1600, 1587, 1504, 1264, 846, 724; ¹H NMR (400 MHz) 0.87–0.91 (m, 3H, CH₃), 1.26–1.49 (m, 10H, 5 × CH₂), 1.75–1.82 (m, 2H, CH₂), 3.98 (t, 2H, ³*J*_{HH} = 6.5 Hz, OCH₂), 6.87–6.89 (m, 2H, C_{Ar}H), 7.63–7.67 (m, 2H, C_{Ar}H); ¹⁹F NMR (376 MHz) 63.8 (d, 4F, ²*J*_{FF} = 150.0 Hz, SF₄), 85.1–86.7 (m, 1F, SF); ¹³C NMR (100 MHz) 14.0 (s, CH₃), 22.7 (s, CH₂), 26.0 (s, CH₂), 29.1 (s, CH₂), 29.2 (s, CH₂), 29.3 (s, CH₂), 31.8 (s, CH₂), 68.5 (s, OCH₂), 114.0 (s, C_{Ar}H), 127.6 (p, ³*J*_{CF} = 4.6 Hz, C_{Ar}H), 146.5 (p, ²*J*_{CF} = 17.5 Hz, C_{Ar}SF₅), 161.0 (s, C_{Ar}); MS (EI) *m/z* 332 (M⁺, 69%), 313 (23), 220 (100), 112 (63), 83 (57), 71 (71), 70 (57), 57 (94), 55 (48), 43 (83), 41 (68); Calculated for C₁₄H₂₁F₅OS: C 50.59; H 6.37. Found: C 50.86; H 6.54.

Example 5

1-(Benzyloxy)-4-(pentafluorosulfanyl)benzene (3e): Dry benzylalcohol (311 μL, 3 mmol) was added to a stirred solution of *t*-BuOK (337 mg, 3 mmol) in DMF (1.8 mL). Half of the

resulting mixture was added dropwise to a stirred solution of 1-nitro-4-(pentafluorosulfanyl)benzene (**1**) (249 mg, 1 mmol) in DMF (0.5 mL). After ten minutes of stirring at room temperature, the second half of the alkoxide mixture was added dropwise. After total one hour reaction time, saturated aqueous solution of NH_4Cl (15 mL) and water (5 mL) were added and the product was extracted to Et_2O (3×20 mL). The combined organic phase was washed with saturated aqueous solution of NaCl (15 mL), dried with anhydrous MgSO_4 and solvent was removed under reduced pressure. Column chromatography using silica gel (R_f 0.25, hexane) gave product **3e** as a white crystalline solid (298 mg, 96 mol. %). Mp 89.6–90.1 °C; IR (film, ν_{max} cm^{-1}) 3113, 3084, 3070, 3032, 1599, 1585, 1505, 1490, 1256, 1009, 848, 831, 749, 698; ^1H NMR (400 MHz) 5.08 (s, 2H, CH_2O), 6.95–6.97 (m, 2H, $\text{C}_{\text{Ar}}\text{H}$), 7.32–7.44 (m, 5H, $\text{C}_{\text{Ar}}\text{H}$), 7.64–7.68 (m, 2H, $\text{C}_{\text{Ar}}\text{H}$); ^{19}F NMR (376 MHz) 63.8 (d, 4F, $^2J_{\text{FF}} = 150.1$ Hz, SF_4), 84.6–86.5 (m, 1F, SF); ^{13}C NMR (100 MHz) 70.4 (s, OCH_2), 114.4 (s, $\text{C}_{\text{Ar}}\text{H}$), 127.4 (s, $\text{C}_{\text{Ar}}\text{H}$), 127.6 (p, $^3J_{\text{CF}} = 4.6$ Hz, $\text{C}_{\text{Ar}}\text{H}$), 128.3 (s, $\text{C}_{\text{Ar}}\text{H}$), 128.7 (s, $\text{C}_{\text{Ar}}\text{H}$), 136.0 (s, C_{Ar}), 146.8 (p, $^2J_{\text{CF}} = 17.6$ Hz, $\text{C}_{\text{Ar}}\text{SF}_5$), 160.5 (s, C_{Ar}); MS (EI) m/z 310 (M^+ , 5%), 291 (3), 91 (100), 65 (11); Calculated for $\text{C}_{13}\text{H}_{11}\text{F}_5\text{OS}$: C 50.32; H 3.57; F 30.61; S 10.33. Found: C 50.34; H 3.50; F 30.49; S 10.51.

Example 6

1-Phenethoxy-4-(pentafluorosulfanyl)benzene (3f): Dry 2-phenylethanol (330 μL , 3 mmol) was added to a stirred solution of *t*-BuOK (337 mg, 3 mmol) in DMF (2.5 mL). Half of the resulting mixture was added dropwise to a stirred solution of 1-nitro-4-(pentafluorosulfanyl)benzene (**1**) (249 mg, 1 mmol) in DMF (0.5 mL). After ten minutes of stirring at room temperature, the second half of the alkoxide mixture was added dropwise. After total 30 minutes reaction time, saturated aqueous solution of NH_4Cl (15 mL) and water (5 mL) were added and the product was extracted to Et_2O (3×20 mL). The combined organic phase was washed with saturated aqueous solution of NaCl (15 mL), dried with anhydrous MgSO_4 and solvent was removed under reduced pressure. Column chromatography using silica gel (R_f 0.39, hexane) gave product **3f** as a colorless liquid (204 mg, 63 mol. %). IR (film, ν_{max} cm^{-1}) 3110, 3088, 3031, 2933, 2876, 1600, 1587, 1504, 1263, 828, 751; ^1H NMR (400 MHz) 3.10 (t, 2H, $^3J_{\text{HH}} = 7.0$ Hz, CH_2), 4.19 (t, 2H, $^3J_{\text{HH}} = 7.0$ Hz, CH_2O), 6.87–6.89 (m, 2H, $\text{C}_{\text{Ar}}\text{H}$), 7.23–7.34 (m, 5H, $\text{C}_{\text{Ar}}\text{H}$), 7.63–7.67 (m, 2H, $\text{C}_{\text{Ar}}\text{H}$); ^{19}F NMR (376 MHz) 63.8 (d, 4F, $^2J_{\text{FF}} = 150.0$ Hz, SF_4), 84.9–86.5 (m, 1F, SF); ^{13}C NMR (100 MHz) 35.6 (s, CH_2), 69.1 (s, OCH_2), 114.4 (s, $\text{C}_{\text{Ar}}\text{H}$), 126.7 (s, $\text{C}_{\text{Ar}}\text{H}$), 127.6 (p, $^3J_{\text{CF}} = 4.6$ Hz, $\text{C}_{\text{Ar}}\text{H}$), 128.6 (s, $\text{C}_{\text{Ar}}\text{H}$),

128.9 (s, $C_{Ar}H$), 137.7 (s, C_{Ar}), 146.7 (p, ${}^2J_{CF} = 16.7$ Hz, $C_{Ar}SF_5$), 160.6 (s, C_{Ar}); MS (EI) m/z 324 (M^+ , 13%), 305 (4), 105 (100), 91 (13), 79 (12), 77 (13); Calculated for $C_{14}H_{13}F_5OS$: C 51.85; H 4.04; S 9.89. Found: C 52.21; H 4.31; S 9.81.

Example 7

1-(Pentafluorosulfanyl)-4-(2,2,2-trifluoroethoxy)benzene (3g): Trifluoroethanol (1.0 mL, 13.7 mmol) was added to a mixture of sodium (81 mg, 3.52 mmol) in THF (7 mL). The mixture was stirred until all sodium reacted. Solvent and excess of trifluoroethanol were removed under reduced pressure and DMF (2 mL) was added to the resulting white solid. A solution of 1-nitro-4-(pentafluorosulfanyl)benzene (**1**) (249 mg, 1 mmol) in DMF (1.5 mL) was added resulting in formation of dark reaction mixture. After total reaction time of three hours, saturated aqueous solution of NH_4Cl (15 mL) and water (5 mL) were added and the product was extracted to Et_2O (3×20 mL). The combined organic phase was washed with saturated aqueous solution of $NaCl$ (15 mL), dried with anhydrous $MgSO_4$ and solvent was removed under reduced pressure. Column chromatography using silica gel (R_f 0.39, hexane) gave product **3g** as a colorless liquid (208 mg, 69 mol. %). IR (film, ν_{max} cm^{-1}) 3122, 3092, 2952, 2902, 1600, 1594, 1505, 1251, 1170, 844; 1H NMR (400 MHz) 4.40 (q, 2H, ${}^3J_{HF} = 7.9$ Hz, OCH_2), 6.97–6.99 (m, 2H, $C_{Ar}H$), 7.72–7.74 (m, 2H, $C_{Ar}H$); ${}^{19}F$ NMR (376 MHz) –74.3 (t, 2F, ${}^3J_{FH} = 7.9$ Hz, CF_3), 63.4 (d, 4F, ${}^2J_{FF} = 150.2$ Hz, SF_4), 83.7–85.3 (m, 1F, SF); ${}^{13}C$ NMR (100 MHz) 65.8 (q, ${}^2J_{CF} = 36.3$ Hz, OCH_2), 114.5 (s, $C_{Ar}H$), 123.0 (q, ${}^1J_{CF} = 278.0$ Hz, CF_3), 128.0 (p, ${}^3J_{CF} = 4.7$ Hz, $C_{Ar}H$), 147.8–148.5 (m, $C_{Ar}SF_5$), 158.9 (s, C_{Ar}); MS (EI) m/z 302 (M^+ , 100%), 283 (14), 194 (25), 156 (17), 111 (47), 83 (29); Calculated for $C_8H_6F_8OS$: C 31.80; H 2.00. Found: C 32.04; H 2.01.

Example 8

2,2-Dimethyl-4-((4-(pentafluorosulfanyl)phenoxy)methyl)-1,3-dioxolane (3h): 1,2-Isopropylidenglycerol (421 μ L, 3.3 mmol) was added to a stirred solution of *t*-BuOK (337 mg, 3.0 mmol) in DMF (3.5 mL). The resulting solution was added to a solution of 1-nitro-4-(pentafluorosulfanyl)benzene (**1**) (249 mg, 1 mmol) in DMF (1 mL) and the mixture was stirred for 30 min at room temperature. Next, saturated aqueous solution of NH_4Cl (15 mL) and water (5 mL) were added and the product was extracted to Et_2O (3×20 mL). The combined organic phase was washed with saturated aqueous solution of $NaCl$ (15 mL), dried with anhydrous $MgSO_4$ and solvent was removed under reduced pressure. Column

chromatography using silica gel (R_f 0.12, 5 vol. % of ethyl acetate in hexane) gave product **3h** as a white crystalline solid (194 mg, 58 mol. %). Mp 78.6–79.1 °C; IR (film, ν_{\max} cm^{-1}) 3073, 2992, 2923, 1600, 1588, 1504, 1490, 1377, 836; ^1H NMR (400 MHz) 1.41 (s, 3H, CH_3), 1.46 (s, 3H, CH_3), 3.88–4.20 (m, 5H, $2 \times \text{CH}_2\text{O}$), 4.49 (p, $^3J_{\text{HH}} = 5.9$ Hz, CHO), 6.92–6.95 (m, 2H, $\text{C}_{\text{Ar}}\text{H}$), 7.67–7.69 (m, 2H, $\text{C}_{\text{Ar}}\text{H}$); ^{19}F NMR (376 MHz) 63.7 (d, 4F, $^2J_{\text{FF}} = 150.1$ Hz, SF_4), 84.6–86.2 (m, 1F, SF); ^{13}C NMR (100 MHz) 25.3 (s, CH_3), 26.8 (s, CH_3), 66.6 (s, CH_2O), 69.1 (s, CH_2O), 73.7 (s, CHO), 110.0 (s, CMe_2), 114.1 (s, $\text{C}_{\text{Ar}}\text{H}$), 127.7 (p, $^3J_{\text{CF}} = 4.6$ Hz, $\text{C}_{\text{Ar}}\text{H}$), 146.9–147.4 (m, $\text{C}_{\text{Ar}}\text{SF}_5$), 160.3 (s, C_{Ar}); MS (EI) m/z 334 (M^+ , 5%), 321 (13), 319 (100), 259 (16), 132 (55), 131 (34), 101 (63), 43 (69); Calculated for $\text{C}_{12}\text{H}_{15}\text{F}_5\text{O}_3\text{S}$: C 43.11; H 4.52; F 28.41; S 9.59. Found: C 43.28; H 4.46; F 27.72; S 8.95.

Example 9

1-Isopropoxy-4-(pentafluorosulfanyl)benzen (3i): Dry 2-propanol (276 μL , 3.60 mmol) was added to a stirred solution of *t*-BuOK (405 mg, 3.60 mmol) in DMF (1.7 mL). Half of the resulting mixture was added dropwise to a stirred solution of 1-nitro-4-(pentafluorosulfanyl)benzene (**1**) (299 mg, 1.2 mmol) in DMF (0.5 mL). After 20 minutes of stirring at room temperature, the second half of the alkoxide mixture was added dropwise. After total reaction time of 90 minutes, saturated aqueous solution of NH_4Cl (15 mL) and water (5 mL) were added and the product was extracted to Et_2O (3×20 mL). The combined organic phase was washed with saturated aqueous solution of NaCl (15 mL), dried with anhydrous MgSO_4 and solvent was removed under reduced pressure. Column chromatography using silica gel (R_f 0.38, hexane) gave product **3i** as a colorless liquid (167 mg, 53 mol. %). IR (film, ν_{\max} cm^{-1}) 3115, 3053, 2983, 2937, 1599, 1588, 1503, 1388, 1377, 1264, 1192, 1103, 953, 835, 782; ^1H NMR (400 MHz) 1.35 (d, 6H, $^3J_{\text{HH}} = 6.1$ Hz, $\text{CH}(\text{CH}_3)_2$), 4.59 (septet, 1H, $^3J_{\text{HH}} = 6.1$ Hz, OCH), 6.86–6.88 (m, 2H, $\text{C}_{\text{Ar}}\text{H}$), 7.64–7.67 (m, 2H, $\text{C}_{\text{Ar}}\text{H}$); ^{19}F NMR (376 MHz) 63.8 (d, 4F, $^2J_{\text{FF}} = 150.0$ Hz, SF_4), 85.1–86.7 (m, 1F, SF); ^{13}C NMR (100 MHz) 21.8 (s, CH_3), 70.4 (s, OCH), 114.9 (s, $\text{C}_{\text{Ar}}\text{H}$), 127.6 (p, $^3J_{\text{CF}} = 4.6$ Hz, $\text{C}_{\text{Ar}}\text{H}$), 146.3 (p, $^2J_{\text{CF}} = 17.5$ Hz, $\text{C}_{\text{Ar}}\text{SF}_5$), 159.9 (s, C_{Ar}); MS (EI) m/z 262 (M^+ , 18%), 220 (100), 112 (52), 43 (14).

Example 10

1-Phenoxy-4-(pentafluorosulfanyl)benzene (3j): Solution of potassium phenolate (456 mg, 3.45 mmol) in DMF (2.5 mL) was added over one hour to a stirred solution of 1-nitro-4-

(pentafluorosulfanyl)benzene (**1**) (172 mg, 0.69 mmol) in DMF (1 mL) at room temperature. After total reaction time of 17 hours, saturated aqueous solution of NH_4Cl (15 mL) and water (5 mL) were added and the product was extracted to Et_2O (3×20 mL). The combined organic phase was washed with saturated aqueous solution of NaCl (15 mL), dried with anhydrous MgSO_4 and solvent was removed under reduced pressure. Column chromatography using silica gel (R_f 0.33, hexane) gave product **3j** as a colorless liquid (120 mg, 59 mol. %). IR (film, ν_{max} cm^{-1}) 1582, 1498, 1489, 1255, 1244, 825, 753, 695; ^1H NMR (400 MHz) 6.97–7.00 (m, 2H, $\text{C}_{\text{Ar}}\text{H}$), 7.05–7.08 (m, 2H, $\text{C}_{\text{Ar}}\text{H}$), 7.19–7.25 (m, 1H, $\text{C}_{\text{Ar}}\text{H}$), 7.38–7.43 (m, 2H, $\text{C}_{\text{Ar}}\text{H}$), 7.67–7.71 (m, 2H, $\text{C}_{\text{Ar}}\text{H}$); ^{19}F NMR (376 MHz) 63.5 (d, 4F, $^2J_{\text{FF}} = 150.1$ Hz, SF_4), 84.1–85.7 (m, 1F, SF); ^{13}C NMR (100 MHz) 117.2 (s, $\text{C}_{\text{Ar}}\text{H}$), 120.1 (s, $\text{C}_{\text{Ar}}\text{H}$), 124.8 (s, $\text{C}_{\text{Ar}}\text{H}$), 127.8 (p, $^3J_{\text{CF}} = 4.7$ Hz, $\text{C}_{\text{Ar}}\text{H}$), 130.1 (s, $\text{C}_{\text{Ar}}\text{H}$), 148.1 (p, $^2J_{\text{CF}} = 18.1$ Hz, $\text{C}_{\text{Ar}}\text{SF}_5$), 155.4 (s, C_{Ar}), 160.0 (s, C_{Ar}); MS (EI) m/z 297 ($\text{M}+1$, 14%), 296 (M^+ , 100), 277 (5), 188 (10), 169 (9), 159 (12), 141 (12), 115 (12), 77 (36), 51 (11).

Example 11

Methyl(4-(pentafluorosulfanyl)phenyl)sulfide (3k): Sodium methanethiolate (381 mg, 5.44 mmol, 3 eq.) was added in three portions over 5 minute intervals to a stirred solution of 1-nitro-4-(pentafluorosulfanyl)benzene (**1**) (452 mg, 1.81 mmol, 1 eq.) in DMF (2.2 mL) at room temperature. After total reaction time of 16 hours, saturated aqueous solution of NH_4Cl (20 mL) and water (10 mL) were added and the product was extracted to Et_2O (3×25 mL). The combined organic phase was washed with saturated aqueous solution of NaCl (20 mL), dried with anhydrous MgSO_4 and solvent was removed under reduced pressure. Column chromatography using silica gel (R_f 0.50, hexane) gave product **3k** as a colorless liquid (292 mg, 64 mol. %). IR (film, ν_{max} cm^{-1}) 3078, 3064, 2992, 2928, 1593, 1579, 1488, 1475, 1437, 1401, 1085, 835, 735; ^1H NMR (400 MHz) 2.50 (s, 3H, CH_3), 7.22–7.26 (m, 2H, $\text{C}_{\text{Ar}}\text{H}$), 7.61–7.65 (m, 2H, $\text{C}_{\text{Ar}}\text{H}$); ^{19}F NMR (376 MHz) 62.9 (d, 4F, $^2J_{\text{FF}} = 150.1$ Hz, SF_4), 83.9–85.5 (m, 1F, SF); ^{13}C NMR (100 MHz) 14.9 (s, CH_3), 125.1 (s, $\text{C}_{\text{Ar}}\text{H}$), 126.2 (p, $^3J_{\text{CF}} = 4.7$ Hz, $\text{C}_{\text{Ar}}\text{H}$), 144.1 (s, C_{Ar}), 150.5 (p, $^2J_{\text{CF}} = 17.6$ Hz, $\text{C}_{\text{Ar}}\text{SF}_5$); MS (EI) m/z 250 (M^+ , 100%), 142 (24), 127 (34), 108 (10), 83 (10), 45 (12).

Example 12

***n*-Octyl(4-(pentafluorosulfanyl)phenyl)sulfide (3l)**: *n*-Octanethiol (178 μL , 1.08 mmol) was added to a stirred solution of *t*-BuOK (146 mg, 1.3 mmol) in DMF (3 mL). To the resulting

solution a solution of 1-nitro-4-(pentafluorosulfanyl)benzene (**1**) (541 mg, 2.17 mmol) in DMF (2 mL) was added at room temperature. After one hour, saturated aqueous solution of NH_4Cl (15 mL) and water (5 mL) were added and the product was extracted to Et_2O (3×20 mL). The combined organic phase was washed with saturated aqueous solution of NaCl (15 mL), dried with anhydrous MgSO_4 and solvent was removed under reduced pressure. Column chromatography using silica gel (R_f 0.64, hexane) gave product **31** as a colorless liquid (162 mg, 43 mol. %). IR (film, ν_{max} cm^{-1}) 2956, 2929, 2857, 1583, 1488, 1468, 1400, 1084, 837; ^1H NMR (400 MHz) 0.86–0.90 (m, 3H, CH_3), 1.22–1.34 (m, 8H, $4 \times \text{CH}_2$), 1.40–1.48 (m, 2H, CH_2), 1.65–1.72 (m, 2H, CH_2), 2.94–2.98 (m, 2H, SCH_2), 7.27–7.29 (m, 2H, $\text{C}_{\text{Ar}}\text{H}$), 7.60–7.64 (m, 2H, $\text{C}_{\text{Ar}}\text{H}$); ^{19}F NMR (376 MHz) 62.8 (d, 4F, $^2J_{\text{FF}} = 150.1$ Hz, SF_4), 83.8–85.4 (m, 1F, SF); ^{13}C NMR (100 MHz) 14.0 (s, CH_3), 22.6 (s, CH_2), 28.7 (s, CH_2), 28.8 (s, CH_2), 29.1 (s, CH_2), 29.1 (s, CH_2), 31.8 (s, CH_2), 32.3 (s, CH_2), 126.2 (p, $^3J_{\text{CF}} = 4.7$ Hz, $\text{C}_{\text{Ar}}\text{H}$), 126.6 (s, $\text{C}_{\text{Ar}}\text{H}$), 143.1 (s, C_{Ar}), 150.7 (p, $^2J_{\text{CF}} = 17.5$ Hz, $\text{C}_{\text{Ar}}\text{SF}_5$); MS (EI) m/z 350 (6 %), 349 (10), 348 (M^+ , 57), 249 (6), 238 (9), 237 (9), 236 (100), 122 (18), 83 (8), 71 (10), 69 (12), 57 (16), 55 (13), 43 (19), 41 (20).

Example 13

***t*-Butyl(4-(pentafluorosulfanyl)phenyl)sulfide (3m)**: *t*-BuSNa (274 mg, 2.44 mmol, 3 eq.) was added in three minutes to a stirred solution of 1-nitro-4-(pentafluorosulfanyl)benzene (**1**) (203 mg, 0.82 mmol, 1 eq.) in DMF (1.2 mL) at room temperature. After reaction time of one hour, saturated aqueous solution of NH_4Cl (15 mL) and water (5 mL) were added and the product was extracted to Et_2O (3×20 mL). The combined organic phase was washed with saturated aqueous solution of NaCl (15 mL), dried with anhydrous MgSO_4 and solvent was removed under reduced pressure. Column chromatography using silica gel (R_f 0.52, hexane) gave a mixture of product **3m** and *t*-BuSSBu-*t* as a colorless liquid (165 mg, corresponding to 33 mg of pure **3m**, 14 mol. %). ^1H NMR (400 MHz) 1.31 (s, 9H, $\text{C}(\text{CH}_3)_3$), 7.58–7.63 (m, 2H, $\text{C}_{\text{Ar}}\text{H}$), 7.68–7.72 (m, 2H, $\text{C}_{\text{Ar}}\text{H}$); ^{19}F NMR (376 MHz) 62.4 (d, 4F, $^2J_{\text{FF}} = 150.0$ Hz, SF_4), 82.7–84.3 (m, 1F, SF); MS (EI) m/z 292 (M^+ , 13%), 236 (39), 127 (14), 83 (13), 57 (100), 41 (28).

Example 14

1-Methoxy-3-(pentafluorosulfanyl)benzene (4a): Sodium methanolate (95 mg, 1.76 mmol, 1.5 eq.) was added to a stirred solution of 1-nitro-3-(pentafluorosulfanyl)benzene (**2**) (292 mg,

1.17 mmol, 1 eq.) in DMF (1.17 mL) at room temperature. After 30 and 90 minutes further amount of sodium methoxide (2×95 mg, 2×1.5 eq.) was added. After total reaction time of 5 hours, saturated aqueous solution of NH_4Cl (15 mL) and water (5 mL) were added and the product was extracted to *t*-BuOMe (3×20 mL). The combined organic phase was washed with saturated aqueous solution of NaCl (15 mL), dried with anhydrous MgSO_4 and solvent was removed under reduced pressure. Column chromatography using silica gel (R_f 0.45, hexane) gave product **4a** as a colorless liquid (144 mg, 52 mol. %). IR (film, ν_{max} cm^{-1}) 3013, 2947, 2842, 1606, 1586, 1494, 1485, 1249, 1040, 840, 791; ^1H NMR (400 MHz) 3.84 (s, 3H, OCH_3), 7.02–7.04 (m, 1H, $\text{C}_{\text{Ar}}\text{H}$), 7.27–7.28 (m, 1H, $\text{C}_{\text{Ar}}\text{H}$), 7.32–7.39 (m, 2H, $\text{C}_{\text{Ar}}\text{H}$); ^{19}F NMR (376 MHz) 62.2 (d, 4F, $^2J_{\text{FF}} = 149.7$ Hz, SF_4), 83.2–84.8 (m, 1F, SF); ^{13}C NMR (100 MHz) 55.6 (s, OCH_3), 112.2 (p, $^3J_{\text{CF}} = 4.8$ Hz, $\text{C}_{\text{Ar}}\text{H}$), 117.1 (s, $\text{C}_{\text{Ar}}\text{H}$), 118.1 (p, $^3J_{\text{CF}} = 4.8$ Hz, $\text{C}_{\text{Ar}}\text{H}$), 129.4 (s, $\text{C}_{\text{Ar}}\text{H}$), 154.5–155.0 (m, $\text{C}_{\text{Ar}}\text{SF}_5$), 159.4 (s, C_{Ar}); MS (EI) m/z 234 (M^+ , 100%), 126 (10), 111 (17), 107 (24), 96 (17), 92 (30), 83 (16), 77 (38), 64 (13), 63 (15); Calculated for $\text{C}_7\text{H}_7\text{F}_5\text{OS}$: C 35.90; H 3.01; S 13.69. Found: C 36.20; H 3.21; S 13.76.

Example 15

1-(*n*-Propoxy)-3-(pentafluorosulfanyl)benzene (4b): Dry 1-propanol (612 μL , 8.19 mmol) was added to a stirred solution of *t*-BuOK (766 mg, 6.83 mmol) in DMF (3 mL). The resulting solution was added dropwise over 15 minutes to a stirred solution of 1-nitro-3-(pentafluorosulfanyl)benzene (**2**) (340 mg, 1.37 mmol) in DMF (1 mL). After total reaction time of one hour, saturated aqueous solution of NH_4Cl (25 mL) and water (15 mL) were added and the product was extracted to Et_2O (3×25 mL). The combined organic phase was washed with water (25 mL), saturated aqueous solution of NaCl (25 mL), dried with anhydrous MgSO_4 and solvent was removed under reduced pressure. Column chromatography using silica gel (R_f 0.53, hexane) gave product **4b** as a colorless liquid (147 mg, 41 mol. %). IR (film, ν_{max} cm^{-1}) 3083, 2971, 2942, 2883, 2860, 1606, 1586, 1493, 1485, 1473, 1446, 1434, 1393, 1256, 1247, 843, 685, 647, 598; ^1H NMR (400 MHz) 1.05 (t, 3H, $^3J_{\text{HH}} = 7.5$ Hz, CH_3), 1.78–1.86 (m, 2H, CH_2), 3.94 (t, 2H, $^3J_{\text{HH}} = 6.5$ Hz, OCH_2), 7.00–7.03 (m, 1H, $\text{C}_{\text{Ar}}\text{H}$), 7.28–7.30 (m, 1H, $\text{C}_{\text{Ar}}\text{H}$), 7.31–7.36 (m, 2H, $\text{C}_{\text{Ar}}\text{H}$); ^{19}F NMR (376 MHz) 62.2 (d, 4F, $^2J_{\text{FF}} = 149.7$ Hz, SF_4), 83.3–84.9 (m, 1F, SF); ^{13}C NMR (100 MHz) 10.4 (s, CH_3), 22.5 (s, CH_2), 70.1 (s, OCH_2), 112.8 (p, $^3J_{\text{CF}} = 4.8$ Hz, $\text{C}_{\text{Ar}}\text{H}$), 117.5 (s, $\text{C}_{\text{Ar}}\text{H}$), 117.9 (p, $^3J_{\text{CF}} = 4.8$ Hz, $\text{C}_{\text{Ar}}\text{H}$), 129.3 (s, $\text{C}_{\text{Ar}}\text{H}$), 154.8 (p, $^2J_{\text{CF}} = 17.5$ Hz, $\text{C}_{\text{Ar}}\text{SF}_5$), 159.0 (s, C_{Ar}); MS (EI) m/z 262 (M^+ , 25%), 220 (100), 135 (8), 112 (19), 43 (16).

Example 16

1-(Benzyloxy)-3-(pentafluorosulfanyl)benzene (4c): Dry benzylalcohol (605 μL , 5.84 mmol) was added to a stirred solution of *t*-BuOK (655 mg, 5.84 mmol) in DMF (4 mL). One fifth of the resulting solution was added to a solution of 1-nitro-3-(pentafluorosulfanyl)benzene (**2**) (291 mg, 1.17 mmol) in DMF (0.6 mL) every 20 minutes. After total reaction time of 150 minutes, saturated aqueous solution of NH_4Cl (15 mL) and water (5 mL) were added and the product was extracted to Et_2O (3×20 mL). The combined organic phase was washed with saturated aqueous solution of NaCl (15 mL), dried with anhydrous MgSO_4 and solvent was removed under reduced pressure. Column chromatography using silica gel (R_f 0.21, hexane) gave product **4c** as a colorless liquid (152 mg, 42 mol. %). IR (film, ν_{max} cm^{-1}) 3092, 3069, 3036, 2931, 2875, 1602, 1584, 1492, 1482, 1245, 839, 799, 737, 697, 684, 648, 597; ^1H NMR (400 MHz) 5.05 (s, 2H, CH_2O), 7.05–7.09 (m, 1H, C_{ArH}), 7.31–7.43 (m, 8H, C_{ArH}); ^{19}F NMR (376 MHz) 62.2 (d, 4F, $^2J_{\text{FF}} = 149.8$ Hz, SF_4), 83.2–84.8 (m, 1F, SF); ^{13}C NMR (100 MHz) 70.6 (s, OCH_2), 113.3 (p, $^3J_{\text{CF}} = 4.8$ Hz, C_{ArH}), 117.8 (s, C_{ArH}), 118.4 (p, $^3J_{\text{CF}} = 4.7$ Hz, C_{ArH}), 127.6 (s, C_{ArH}), 128.3 (s, C_{ArH}), 128.7 (s, C_{ArH}), 129.4 (s, C_{ArH}), 136.0 (s, C_{Ar}), 154.8 (p, $^2J_{\text{CF}} = 17.5$ Hz, C_{ArSF_5}), 158.5 (s, C_{Ar}); MS (EI) m/z 310 (M^+ , 4%), 92 (9), 91 (100), 65 (11).

Example 17**3-(4-(Pentafluorosulfanyl)phenoxy)propane-1,2-diol (5):**

2,2-Dimethyl-4-((4-(pentafluorosulfanyl)phenoxy)methyl)-1,3-dioxolane (**3h**) (171 mg, 0.51 mmol) was dissolved in methanol (5 mL) and catalytic amount of iodine was added. The solution was stirred for 48 hours at room temperature followed by removal of the solvent under reduced pressure. Water (20 mL) and a few drops of saturated aqueous solution of sodium thiosulfide for the removal of iodine were added and the product was extracted into ethyl acetate (3×20 mL). The combined organic phase was washed with saturated aqueous solution of NaCl (15 mL), dried with anhydrous MgSO_4 and solvent was removed under reduced pressure. Column chromatography using silica gel (R_f 0.35, 20 vol. % of ethyl acetate in hexane) gave product **5** as a pale yellow solid (147 mg, 97 mol. %). Mp 73.5–74.0 $^\circ\text{C}$; IR (film, ν_{max} cm^{-1}) 3270, 2943, 2885, 1602, 1589, 1505, 1265, 1102, 1043, 850, 826, 805; ^1H NMR (400 MHz) 3.34 (br s, 1H, OH), 3.71–3.76 (m, 2H, CH_2), 3.81–3.85 (m, 1H, CH), 4.02–4.04 (m, 2H, CH_2), 4.12 (br s, 1H, OH), 6.87–6.90 (m, 2H, C_{ArH}), 7.63–7.65 (m, 2H, C_{ArH}); ^{19}F NMR (376 MHz) 63.7 (d, 4F, $^2J_{\text{FF}} = 150.0$ Hz, SF_4), 84.6–86.2 (m, 1F, SF); ^{13}C NMR

(100 MHz) 63.5 (s, CH₂), 69.3 (s, CH₂), 70.3 (s, CHO), 114.0 (s, C_{Ar}H), 127.7 (p, ³J_{CF} = 4.6 Hz, C_{Ar}H), 147.1 (p, ²J_{CF} = 17.7 Hz, C_{Ar}SF₅), 160.1 (s, C_{Ar}); Calculated for C₉H₁₁F₅O₃S: C 36.74; H 3.77; S 10.90; F 32.28. Found: C 36.91; H 3.72; S 10.85; F 32.11.

Example 18

4-(Pentafluorosulfanyl)phenol: 1-Octanethiol (246 mg, 1.68 mmol) was added to a stirred solution of *t*-BuOK (189 mg, 1.68 mmol) in DMF (3.5 mL) at room temperature. After 10 minutes 1-methoxy-4-(pentafluorosulfanyl)benzene (**3a**) (264 mg, 1.13 mmol) was added and the reaction mixture was heated to 110 °C for one hour. The solution was then cooled to room temperature and poured to water (25 mL). Aqueous solution of hydrochloric acid (36 hm. %) was added to pH 1 and the product was extracted to ethyl acetate (3 × 20 mL). The combined organic phase was washed with saturated aqueous solution of NaCl (15 mL), dried with anhydrous MgSO₄ and solvent was removed under reduced pressure. Column chromatography using silica gel (*R_f* 0.10, 10 vol. % of ethyl acetate in hexane) gave product 4-(pentafluorosulfanyl)phenol as a colorless solid (230 mg, 93 mol. %). Mp 104.6–105.8 °C; IR (film, ν_{max} cm⁻¹) 3239, 1612, 1505, 1446, 1232, 1099, 845, 836, 828; ¹H NMR (400 MHz) 6.15 (br s, 1H, OH), 6.84–6.86 (m, 2H, C_{Ar}H), 7.62–7.65 (m, 2H, C_{Ar}I); ¹⁹F NMR (376 MHz) 63.7 (d, 4F, ²J_{FF} = 150.0 Hz, SF₄), 84.9–86.4 (m, 1F, SF); ¹³C NMR (150.9 MHz) 115.0 (s, C_{Ar}H), 127.8 (p, ³J_{CF} = 4.5 Hz, C_{Ar}H), 146.5 (p, ²J_{CF} = 17.7 Hz, C_{Ar}SF₅), 158.1 (s, C_{Ar}); MS (EI) *m/z* 222 (5%), 221 (8), 220 (M⁺, 100), 201 (11), 112 (72), 93 (20), 89 (11), 84 (16), 65 (34), 63 (17).

Example 19

3-(Pentafluorosulfanyl)phenol: 1-Octanethiol (273 mg, 1.57 mmol) was added to a stirred solution of *t*-BuOK (176 mg, 1.57 mmol) in DMF (2 mL) at room temperature. After 10 minutes 1-methoxy-3-(pentafluorosulfanyl)benzene (**4a**) (245 mg, 1.05 mmol) was added and the reaction mixture was heated to 110 °C for one hour. The solution was then cooled to room temperature and poured to water (25 mL). Aqueous solution of hydrochloric acid (36 hm. %) was added to pH 1 and the product was extracted to ethyl acetate (3 × 20 mL). The combined organic phase was washed with saturated aqueous solution of NaCl (15 mL), dried with anhydrous MgSO₄ and solvent was removed under reduced pressure. Column chromatography using silica gel (*R_f* 0.17, 10 vol. % of ethyl acetate in hexane) gave product 3-(pentafluorosulfanyl)phenol as a colorless liquid (226 mg, 98 mol. %). IR (film, ν_{max} cm⁻¹)

3609, 3364, 1610, 1599, 1482, 1456, 1260, 1238, 840, 805; ^1H NMR (400 MHz) 6.38 (br s, 1H, OH), 6.97–7.00 (m, 1H, $\text{C}_{\text{Ar}}\text{H}$), 7.25–7.27 (m, 1H, $\text{C}_{\text{Ar}}\text{H}$), 7.29–7.33 (m, 2H, $\text{C}_{\text{Ar}}\text{H}$); ^{19}F NMR (376 MHz) 62.2 (d, 4F, $^2J_{\text{FF}} = 149.8$ Hz, SF_4), 83.1–84.7 (m, 1F, SF); ^{13}C NMR (100 MHz) 113.5 (p, $^3J_{\text{CF}} = 4.7$ Hz, $\text{C}_{\text{Ar}}\text{H}$), 118.2 (p, $^3J_{\text{CF}} = 4.7$ Hz, $\text{C}_{\text{Ar}}\text{H}$), 118.7 (s, $\text{C}_{\text{Ar}}\text{H}$), 129.6 (s, $\text{C}_{\text{Ar}}\text{H}$), 154.7 (p, $^2J_{\text{CF}} = 17.3$ Hz, $\text{C}_{\text{Ar}}\text{SF}_5$), 155.6 (s, C_{Ar}); MS (EI) m/z 220 (M^+ , 100%), 112 (47), 93 (36), 89 (18), 84 (17), 65 (54), 39 (22).

Example 20

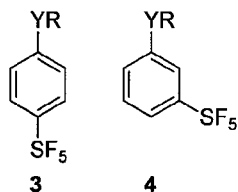
2-Bromo-1-methoxy-4-(pentafluorosulfanyl)benzene (6a): Bromine (0.4 mL, 7.85 mmol, 5 eq.) was added to a solution of 1-methoxy-4-(pentafluorosulfanyl)benzene (**3a**) (368 mg, 1.57 mmol, 1 eq.) in 99 vol. % acetic acid (5.2 mL). The resulting mixture was stirred at 60 °C for 24 hours. Then the mixture was cooled to room temperature and poured to water (45 ml). Saturated aqueous solution of sodium thiosulfate for the reduction of excess of bromine was added followed by the addition of sodium bicarbonate for neutralization of acetic acid. The product was extracted into dichloromethane (3 × 20 ml), the combined organic phase was washed with saturated aqueous solution of NaCl (15 mL), dried with anhydrous MgSO_4 and solvent was removed under reduced pressure. Column chromatography using silica gel (R_f 0.38, 15 vol. % of toluene in hexane) gave the product 2-bromo-1-methoxy-4-(pentafluorosulfanyl)benzene (**6a**) as a colorless liquid (400 mg, 81 mol. %). IR (film, ν_{max} cm^{-1}) 2848, 1590, 1495, 1488, 1303, 1283, 1267, 1112, 1059, 1019, 842; ^1H NMR (400 MHz) 3.93 (s, 3H, OCH_3), 6.88–6.90 (m, 1H, $\text{C}_{\text{Ar}}\text{H}$), 7.66–7.69 (m, 1H, $\text{C}_{\text{Ar}}\text{H}$), 7.94–7.95 (m, 1H, $\text{C}_{\text{Ar}}\text{H}$); ^{19}F NMR (376 MHz) 63.9 (d, 4F, $^2J_{\text{FF}} = 150.5$ Hz, SF_4), 83.5–85.1 (m, 1F, SF); ^{13}C NMR (100 MHz) 56.5 (s, OCH_3), 110.6 (s, $\text{C}_{\text{Ar}}\text{H}$), 111.1 (s, C_{Ar}), 126.5 (p, $^3J_{\text{CF}} = 4.7$ Hz, $\text{C}_{\text{Ar}}\text{H}$), 131.0 (p, $^3J_{\text{CF}} = 4.7$ Hz, $\text{C}_{\text{Ar}}\text{H}$), 146.6 (p, $^2J_{\text{CF}} = 18.6$ Hz, $\text{C}_{\text{Ar}}\text{SF}_5$), 158.0 (s, C_{Ar}); MS (EI) m/z 314 (M^+ , 100%), 312 (M^+ , 100), 206 (12), 204 (12), 191 (35), 189 (35), 172 (10), 170 (10), 163 (23), 161 (23), 89 (13), 75 (18), 63 (27).

Industrial applicability

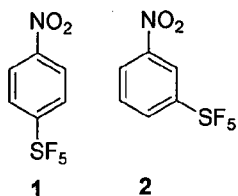
Compounds according to the invention can be used in basic research, chemical industry and in pharmaceutical and agrochemical industry.

CLAIMS

1. A process for the preparation of substituted 3- a 4-(pentafluorosulfanyl)benzenes of general formula 3 and/or 4



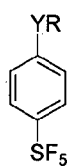
by nucleophilic aromatic substitution characterized in that nitrobenzene having pentafluorosulfanyl group connected in position 3 or 4 of general formula 1 and/or 2,



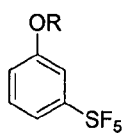
is allowed to react in concentration range $0.01-8 \text{ mol.l}^{-1}$ with compounds RYM^+ , where R is selected from a group comprising saturated, unsaturated, acyclic, cyclic or aromatic, substituted or unsubstituted carbon chain, Y is the element of VI. B group and M^+ is the metal ion, in an organic solvent at temperatures ranging from $-55 \text{ }^\circ\text{C}$ or at least boiling point of the solvent to $150 \text{ }^\circ\text{C}$, giving the corresponding substituted compounds of general formula 3 and/or 4.

2. The process according to claim 1 characterized in that for the preparation of substituted 4-(pentafluorosulfanyl)benzenes of general formula 3 the element Y is preferably selected from a group comprising sulfur and oxygen and for the preparation of substituted 3-(pentafluorosulfanyl)benzenes of general formula 4 the element Y is preferably oxygen.
3. The process according to claim 1 or 2 wherein the metal ion M^+ is selected from a group comprising Na^+ , K^+ or organic cation in advantage tetraalkylammonium.
4. The process according to claim 1, 2 or 3, wherein reactions are in advantage conducted in solvents chosen from a group comprising of dimethylformamide, dimethylsulfoxide, dimethylacetamide and hexamethylphosphoramide.

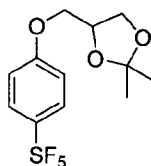
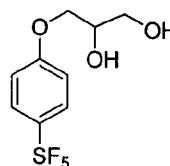
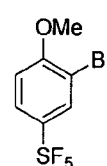
5. The method according to any of the preceding claims, wherein reactions are in advantage conducted in the presence of excess of compound RY^-M^+ .
6. The method according to any of the preceding claims, wherein reactions are in advantage conducted at room temperature in the concentration range of 0.1-4 mol. l^{-1} of starting compound of formula **1** and/or **2**.
7. Use of compounds of general formula **3** for the synthesis of 4-(pentafluorosulfanyl)phenol.
8. Use of compounds of general formula **4** for the synthesis of 3-(pentafluorosulfanyl)phenol.
9. Compounds containing the SF_5 group
 - 1-Ethoxy-4-(pentafluorosulfanyl)benzene of formula **3b**,
 - 1-(*n*-Propoxy)-4-(pentafluorosulfanyl)benzene of formula **3c**,
 - 1-(*n*-Octyloxy)-4-(pentafluorosulfanyl)benzene of formula **3d**,
 - 1-(Benzyloxy)-4-(pentafluorosulfanyl)benzene of formula **3e**,
 - 1-Phnethoxy-4-(pentafluorosulfanyl)benzene of formula **3f**,
 - 1-(Pentafluorosulfanyl)-4-(2,2,2-trifluoroethoxy)benzene of formula **3g**,
 - 2,2-Dimethyl-4-((4-(pentafluorosulfanyl)phenoxy)methyl)-1,3-dioxolane of formula **3h**,
 - 1-Isopropoxy-4-(pentafluorosulfanyl)benzene of formula **3i**,
 - 1-Phenoxy-4-(pentafluorosulfanyl)benzene of formula **3j**,
 - Methyl(4-(pentafluorosulfanyl)phenyl)sulfide of formula **3k**,
 - n*-Octyl(4-(pentafluorosulfanyl)phenyl)sulfide of formula **3l**,
 - t*-Butyl(4-(pentafluorosulfanyl)phenyl)sulfide of formula **3m**,
 - 1-Methoxy-3-(pentafluorosulfanyl)benzene of formula **4a**,
 - 1-(*n*-Propoxy)-3-(pentafluorosulfanyl)benzene of formula **4b**,
 - 1-(Benzyloxy)-3-(pentafluorosulfanyl)benzene of formula **4c**,
 - 3-(4-(Pentafluorosulfanyl)phenoxy)propane-1,2-diol of formula **5**, and
 - 2-Bromo-1-methoxy-4-(pentafluorosulfanyl)benzene of formula **6a**



	R	Y
3b	CH ₃ CH ₂	O
3c	<i>n</i> -C ₃ H ₇	O
3d	<i>n</i> -C ₈ H ₁₇	O
3e	C ₆ H ₅ CH ₂	O
3f	C ₆ H ₅ CH ₂ CH ₂	O
3g	CF ₃ CH ₂	O
3i	<i>i</i> -C ₃ H ₇	O
3j	C ₆ H ₅	O
3k	CH ₃	S
3l	<i>n</i> -C ₈ H ₁₇	S
3m	(CH ₃) ₃ C	S

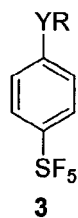
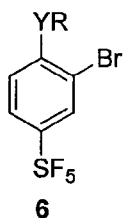


	R
4a	CH ₃
4b	<i>n</i> -C ₃ H ₇
4c	C ₆ H ₅ CH ₂

**3h****5****6a**

which can be used for the development of new biologically active compounds and materials.

10. Use of compounds of general formula 3 for the synthesis of compounds of general formula 6,

**3****6**

wherein compounds of general formula 3 react with brominating reagents in a suitable solvent to give compounds of general formula 6.

INTERNATIONAL SEARCH REPORT

International application No
PCT/CZ2011/000097

A. CLASSIFICATION OF SUBJECT MATTER

INV. C07C381/00
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, CHEM ABS Data, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2009/028514 A1 (UBE INDUSTRIES [JP]; NISHINO SHIGEYOSHI [JP]; SHIMA HIDETAKA [JP]; OMA) 5 March 2009 (2009-03-05) page 50 - page 52; compounds III-2, III-4 -----	9
X	JP 2009 096740 A (UBE INDUSTRIES) 7 May 2009 (2009-05-07) the whole document -----	7-9
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Further documents are listed in the continuation of Box C.

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INTERNATIONAL SEARCH REPORT

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

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