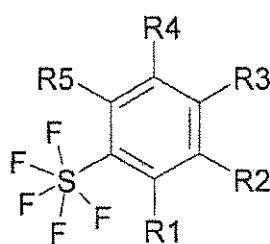


Ortho-substituted pentafluorosulfanyl benzenes, method for the production thereof and their use as synthesis intermediates

- 5 The chemistry of pentafluorosulfanyl derivatives has gained importance in the last few years, especially since novel preparation processes have been found (Tetrahedron 56 (2000) 3399; Organic Letters 4(17) (2002) 3013). However, to date only very few compounds are known which bear substituents other than hydrogen and fluorine on a phenyl ring in the ortho-
- 10 position to the pentafluorosulfanyl group. The only known synthetic route (Journal of Fluorine Chemistry 112 (2001) 287) uses expensive reagents such as AgF_2 and is afflicted with poor yields. The authors account for this by the large bulk of the pentafluorosulfanyl group which generally makes ortho-substitution very difficult. This opinion is also shared by other authors
- 15 (J. Am. Chem. Soc. 84 (1962) 3064). It is therefore surprising that it is possible to electrophilically substitute in the ortho-position to the pentafluorosulfanyl group. In this way, novel ortho-substituted pentafluorosulfanylbenzenes are obtained which constitute valuable intermediates, for example for preparing medicaments, diagnostic aids,
- 20 liquid crystals, pesticides, herbicides, fungicides, nematocides, parasitocides, insecticides, acaricides, arthropodocides and polymers.

The invention relates to pentafluorosulfanylbenzenes of the formula I.

In a first aspect, there is provided a compound of the formula I



25

where

- R1 is Cl, Br, I, -CN, -SO₂R₆, NO₂, alkoxy having 1, 2, 3 or 4 carbon atoms, NR₇R₈, -O-(CH₂)_b-(CF₂)_c-CF₃, -(SO_d)_e-(CH₂)_f-(CF₂)_g-CF₃, alkyl having 1, 2, 3, 4, 5 or 6 carbon atoms or cycloalkyl having 3, 4,
- 30 5, 6, 7 or 8 carbon atoms, in which 1, 2, 3 or 4 hydrogen atoms may be replaced by fluorine atoms;

R₆ is OH, F, Cl, Br, I or alkyl having 1, 2, 3 or 4 carbon atoms;

R7 and R8

are each independently hydrogen, alkyl having 1, 2, 3 or 4 carbon atoms or $-\text{CH}_2\text{-CF}_3$;

b and c

5 are each independently zero or 1;

d is zero, 1 or 2;

e is zero or 1;

f is zero, 1, 2, 3 or 4;

g is zero or 1;

10 or

R1 is $-(\text{CH}_2)_h$ -phenyl or -O-phenyl,

in which the phenyl radicals are unsubstituted or substituted by 1, 2 or 3 radicals selected from the group consisting of F, Cl, Br, I, $-\text{O}_j-(\text{CH}_2)_k\text{-CF}_3$, alkoxy having 1, 2, 3 or 4 carbon atoms, alkyl having 1, 2, 3 or 4 carbon atoms and $-\text{SO}_2\text{CH}_3$;

15

j is zero or 1;

k is zero, 1, 2 or 3;

h is zero, 1, 2, 3 or 4;

or

20 R1 is $-(\text{CH}_2)_l$ -heteroaryl

which is unsubstituted or substituted by 1, 2 or 3 radicals selected from the group consisting of F, Cl, Br, I, $-\text{O}_m-(\text{CH}_2)_n\text{-CF}_3$, alkoxy having 1, 2, 3 or 4 carbon atoms, alkyl having 1, 2, 3 or 4 carbon atoms and $-\text{SO}_2\text{CH}_3$;

25

m is zero or 1;

n is zero, 1, 2 or 3;

l is zero, 1, 2, 3 or 4;

R2 is hydrogen, F, Cl, Br, I, $-\text{CN}$, NR_9R_{10} , $-\text{OR}_{11}$, $-\text{SR}_{12}$, $-\text{COR}_{13}$, $-\text{SO}_q\text{CH}_3$, $-(\text{SO}_r)_s-(\text{CH}_2)_t(\text{CF}_2)_u\text{-CF}_3$, alkyl having 1, 2, 3, 4, 5 or 6 carbon atoms or cycloalkyl having 3, 4, 5, 6, 7 or 8 carbon atoms, in which 1, 2, 3 or 4 hydrogen atoms may be replaced by fluorine atoms;

30

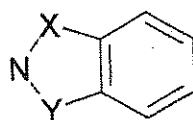
R9, R10, R11 and R12

are each independently hydrogen, alkyl having 1, 2, 3 or 4 carbon atoms, $-(\text{CH}_2)_v(\text{CF}_2)_w\text{-CF}_3$, alkylcarbonyl having 1, 2, 3 or 4 carbon atoms or alkylsulfonyl having 1, 2, 3 or 4 carbon atoms;

35

or

R9 and R10, together with the nitrogen atom bearing them, form a heterocycle of the formula III:



III

X and Y

5 are each independently CO or SO₂;

R13 is OH, alkyl having 1, 2, 3, 4, 5 or 6 carbon atoms or alkoxy having 1, 2, 3, 4, 5 or 6 carbon atoms;

q and r

are each independently 1 or 2;

10 s is zero or 1;

t is zero, 1, 2, 3 or 4;

u is zero or 1;

v is zero, 1, 2, 3 or 4;

w is zero or 1;

15 one of the R3 and R4 radicals

is hydrogen, F, Cl, Br, I, -CN, -NO₂, -COR₁₄, -SO₂CH₃, alkyl having 1, 2, 3, 4, 5 or 6 carbon atoms, alkoxy having 1, 2, 3 or 4 carbon atoms, -O_x-(CH₂)_y-CF₃,

20 R14 is OH, alkyl having 1, 2, 3, 4, 5 or 6 carbon atoms, alkoxy having 1, 2, 3, 4, 5 or 6 carbon atoms or -O_{aa}-(CH₂)_{bb}-CF₃;

x is zero or 1;

y is zero, 1, 2 or 3;

aa is zero or 1;

25 bb is zero, 1, 2 or 3;

and the other of the R3 and R4 radicals

is O_{ss}-phenyl,

in which the phenyl radical is unsubstituted or substituted by 1, 2, 3, 4 or 5 radicals selected from the group consisting of F, Cl, Br, I, NO₂, alkyl having 1, 2, 3 or 4 carbon atoms, -SO_{qq}CH₃, -SO_{rr}CF₃, -CF₃, -OCF₃, -SF₅, -CN or COR₁₃;

30 qq is zero, 1 or 2;

rr is zero, 1 or 2,

ss is zero or 1;

R5 is hydrogen, -NO₂, -SO₂Cl, F, Cl, Br, I, -CN, -SO₂CH₃, alkoxy having 1, 2, 3 or 4 carbon atoms, NR₁₅R₁₆, -O-(CH₂)_{ee}-(CF₂)_{ff}-CF₃, -(SO_{gg})_{hh}-(CH₂)_{jj}-(CF₂)_{kk}-CF₃, alkyl having 1, 2, 3, 4, 5 or 6 carbon atoms or cycloalkyl having 3, 4, 5, 6, 7 or 8 carbon atoms in which 1, 2, 3 or 4 hydrogen atoms may be replaced by fluorine atoms;

R₁₅ and R₁₆

are each independently hydrogen, alkyl having 1, 2, 3 or 4 carbon atoms or -CH₂-CF₃;

ee and ff

are each independently zero or 1;

gg is zero, 1 or 2;

hh is zero or 1;

jj is zero, 1, 2, 3 or 4;

kk is zero or 1;

or

R₅ is -(CH₂)_{ll}-phenyl or -O-phenyl,

in which the phenyl radicals are unsubstituted or substituted by 1, 2 or 3 radicals selected from the group consisting of F, Cl, Br, I, -O_{mm}-(CH₂)_{nn}-CF₃, alkoxy having 1, 2, 3 or 4 carbon atoms, alkyl having 1, 2, 3 or 4 carbon atoms and -SO₂CH₃;

mm is zero or 1;

nn is zero, 1, 2 or 3;

ll is zero, 1, 2, 3 or 4;

25 or

R₅ is -(CH₂)_{oo}-heteroaryl

which is unsubstituted or substituted by 1, 2 or 3 radicals selected from the group consisting of F, Cl, Br, I, -O_{pp}-(CH₂)_{rr}-CF₃, alkoxy having 1, 2, 3 or 4 carbon atoms, alkyl having 1, 2, 3 or 4 carbon atoms and -SO₂CH₃;

pp is zero or 1;

rr is zero, 1, 2 or 3;

oo is zero, 1, 2, 3 or 4;

and salts thereof;

35

Preference is given to compounds of the formula I in which:

R₁ is Cl, Br, I, -CN, -SO₂R₆, NO₂, alkoxy having 1, 2, 3 or 4 carbon atoms, NR₇R₈, -O-(CH₂)_b-(CF₂)_c-CF₃, -(SO_d)_e-(CH₂)_f-(CF₂)_g-CF₃,

alkyl having 1, 2, 3, 4, 5 or 6 carbon atoms or cycloalkyl having 3, 4, 5, 6, 7 or 8 carbon atoms, in which 1, 2, 3 or 4 hydrogen atoms may be replaced by fluorine atoms;

5 R6 is OH, F, Cl, Br, I or alkyl having 1, 2, 3 or 4 carbon atoms;

R7 and R8

are each independently hydrogen, alkyl having 1, 2, 3 or 4 carbon atoms or $-\text{CH}_2\text{-CF}_3$;

b and c

10 are each independently zero or 1;

d is zero, 1 or 2;

e is zero or 1;

f is zero, 1, 2, 3 or 4;

g is zero or 1;

15 or

R1 is $-(\text{CH}_2)_h\text{-phenyl}$ or $-\text{O-phenyl}$,

in which the phenyl radicals are unsubstituted or substituted by 1, 2 or 3 radicals selected from the group consisting of F, Cl, Br, I, $-\text{O}_j\text{-(CH}_2)_k\text{-CF}_3$, alkoxy having 1, 2, 3 or 4 carbon atoms, alkyl having 1, 2, 3 or 4 carbon atoms and $-\text{SO}_2\text{CH}_3$;

20

j is zero or 1;

k is zero, 1, 2 or 3;

h is zero, 1, 2, 3 or 4;

or

25 R1 is $-(\text{CH}_2)_l\text{-heteroaryl}$

which is unsubstituted or substituted by 1, 2 or 3 radicals selected from the group consisting of F, Cl, Br, I, $-\text{O}_m\text{-(CH}_2)_n\text{-CF}_3$, alkoxy having 1, 2, 3 or 4 carbon atoms, alkyl having 1, 2, 3 or 4 carbon atoms and $-\text{SO}_2\text{CH}_3$;

30

m is zero or 1;

n is zero, 1, 2 or 3;

l is zero, 1, 2, 3 or 4;

R2 is hydrogen, F, Cl, Br, I, $-\text{CN}$, NR_9R_{10} , $-\text{OR}_{11}$, $-\text{SR}_{12}$, $-\text{COR}_{13}$, $-\text{SO}_q\text{CH}_3$, $-(\text{SO}_r)_s\text{-(CH}_2)_t\text{-(CF}_2)_u\text{-CF}_3$, alkyl having 1, 2, 3, 4, 5 or 6 carbon atoms or cycloalkyl having 3, 4, 5, 6, 7 or 8 carbon atoms, in which 1, 2, 3 or 4 hydrogen atoms may be replaced by fluorine atoms;

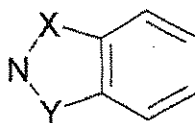
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R9, R10, R11 and R12

are each independently hydrogen, alkyl having 1, 2, 3 or 4 carbon atoms, $-(CH_2)_v-(CF_2)_w-CF_3$, alkylcarbonyl having 1, 2, 3 or 4 carbon atoms or alkylsulfonyl having 1, 2, 3 or 4 carbon atoms;

or

R9 and R10, together with the nitrogen atom bearing them, form a heterocycle of the formula III:



III

X and Y

are each independently CO or SO₂;

R13 is OH, alkyl having 1, 2, 3, 4, 5 or 6 carbon atoms or alkoxy having 1, 2, 3, 4, 5 or 6 carbon atoms;

q and r

are each independently 1 or 2;

s is zero or 1;

t is zero, 1, 2, 3 or 4;

u is zero or 1;

v is zero, 1, 2, 3 or 4;

w is zero or 1;

one of the R3 and R4 radicals

is hydrogen, F, Cl, Br, I, -CN, -NO₂, -COR₁₄, -SO₂CH₃, alkyl having 1, 2, 3, 4, 5 or 6 carbon atoms, alkoxy having 1, 2, 3 or 4 carbon atoms, -O_x-(CH₂)_y-CF₃,

R14 is OH, alkyl having 1, 2, 3, 4, 5 or 6 carbon atoms, alkoxy having 1, 2, 3, 4, 5 or 6 carbon atoms or -O_{aa}-(CH₂)_{bb}-CF₃;

x is zero or 1;

y is zero, 1, 2 or 3;

aa is zero or 1;

bb is zero, 1, 2 or 3;

and the other of the R3 and R4 radicals

is -O-phenyl

in which the phenyl radical is unsubstituted or substituted by 1, 2, 3,

4 or 5 radicals selected from the group consisting of F, Cl, Br, I, NO₂, alkyl having 1, 2, 3 or 4 carbon atoms, -SO_{qq}-CH₃, -SO_{rr}-CF₃, -CF₃, -OCF₃, SF₅, -CN or -COR₁₃;

qq is zero, 1 or 2;

5 rr is zero, 1 or 2;

R5 is hydrogen, -NO₂, -SO₂Cl, F, Cl, Br, I, -CN, -SO₂CH₃, alkoxy having 1, 2, 3 or 4 carbon atoms, NR₁₅R₁₆, -O-(CH₂)_{ee}-(CF₂)_{ff}-CF₃, -(SO_{gg})_{hh}-(CH₂)_{jj}-(CF₂)_{kk}-CF₃, alkyl having 1, 2, 3, 4, 5 or 6 carbon atoms or cycloalkyl having 3, 4, 5, 6, 7 or 8 carbon atoms in which 1, 2, 3 or 4 hydrogen atoms may be replaced by fluorine atoms;

R₁₅ and R₁₆

are each independently hydrogen, alkyl having 1, 2, 3 or 4 carbon atoms or -CH₂-CF₃;

15 ee and ff

are each independently zero or 1;

gg is zero, 1 or 2;

hh is zero or 1;

jj is zero, 1, 2, 3 or 4;

20 kk is zero or 1;

or

R5 is -(CH₂)_{ll}-phenyl or -O-phenyl, in which the phenyl radicals are unsubstituted or substituted by 1, 2 or 3 radicals selected from the group consisting of F, Cl, Br, I, -O_{mm}-(CH₂)_{nn}-CF₃, alkoxy having 1, 2, 3 or 4 carbon atoms, alkyl having 1, 2, 3 or 4 carbon atoms and -SO₂CH₃;

mm is zero or 1;

nn is zero, 1, 2 or 3;

ll is zero, 1, 2, 3 or 4;

30 or

R5 is -(CH₂)_{oo}-heteroaryl which is unsubstituted or substituted by 1, 2 or 3 radicals selected from the group consisting of F, Cl, Br, I, -O_{pp}-(CH₂)_{rr}-CF₃, alkoxy having 1, 2, 3 or 4 carbon atoms, alkyl having 1, 2, 3 or 4 carbon atoms and -SO₂CH₃;

35

pp is zero or 1;

rr is zero, 1, 2 or 3;

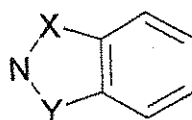
oo is zero, 1, 2, 3 or 4;

and salts thereof;

Particular preference is given to compounds of the formula I in which:

- 5 R1 is Cl, Br, I, -CN, -SO₂R₆, NO₂, alkoxy having 1, 2, 3 or 4 carbon atoms, NR₇R₈, -O-(CH₂)_b-(CF₂)_c-CF₃, -(SO_d)_e-(CH₂)_f(CF₂)_g-CF₃, alkyl having 1, 2, 3, 4, 5 or 6 carbon atoms or cycloalkyl having 3, 4, 5, 6, 7 or 8 carbon atoms, in which 1, 2, 3 or 4 hydrogen atoms may be replaced by fluorine atoms;
- 10 R₆ is OH, F, Cl, Br, I or alkyl having 1, 2, 3 or 4 carbon atoms;
- R₇ and R₈ are each independently hydrogen, alkyl having 1, 2, 3 or 4 carbon atoms or -CH₂-CF₃;
- 15 b and c are each independently zero or 1;
- d is zero, 1 or 2;
- e is zero or 1;
- f is zero, 1, 2, 3 or 4;
- g is zero or 1;
- 20 or
- R1 is -(CH₂)_h-phenyl or -O-phenyl, in which the phenyl radicals are unsubstituted or substituted by 1, 2 or 3 radicals selected from the group consisting of F, Cl, Br, I, -O_j-(CH₂)_k-CF₃, alkoxy having 1, 2, 3 or 4 carbon atoms, alkyl having 1, 2, 3 or 4 carbon atoms and -SO₂CH₃;
- 25 j is zero or 1;
- k is zero, 1, 2 or 3;
- h is zero, 1, 2, 3 or 4;
- or
- 30 R1 is -(CH₂)_l-heteroaryl which is unsubstituted or substituted by 1, 2 or 3 radicals selected from the group consisting of F, Cl, Br, I, -O_m-(CH₂)_n-CF₃, alkoxy having 1, 2, 3 or 4 carbon atoms, alkyl having 1, 2, 3 or 4 carbon atoms and -SO₂CH₃;
- 35 m is zero or 1;
- n is zero, 1, 2 or 3;
- l is zero, 1, 2, 3 or 4;

- R2 is hydrogen, F, Cl, Br, I, -CN, -NR₉R₁₀, -OR₁₁, -SR₁₂, -COR₁₃,
 -(SO_r)_s-(CH₂)_t-(CF₂)_u-CF₃, alkyl having 1, 2, 3, 4, 5 or 6 carbon
 atoms or cycloalkyl having 3, 4, 5, 6, 7 or 8 carbon atoms, in which
 1, 2, 3 or 4 hydrogen atoms may be replaced by fluorine atoms;
- 5 R₉, R₁₀, R₁₁ and R₁₂
 are each independently hydrogen, alkyl having 1, 2, 3
 or 4 carbon atoms, -(CH₂)_v-(CF₂)_w-CF₃, alkylcarbonyl
 having 1, 2, 3 or 4 carbon atoms or alkylsulfonyl having
 1, 2, 3 or 4 carbon atoms;
- 10 or
 R₉ and R₁₀, together with the nitrogen atom bearing them,
 form a heterocycle of the formula III:



III

- X and Y
 15 are each independently CO or SO₂;
- R₁₃ is OH, alkyl having 1, 2, 3, 4, 5 or 6 carbon atoms or
 alkoxy having 1, 2, 3, 4, 5 or 6 carbon atoms;
- s is zero;
- t and u
 20 are each independently zero or 1;
- v and w
 are each independently zero or 1;
- one of the R₃ and R₄ radicals
 is hydrogen, F, Cl, Br, I, -CN, -NO₂, -COR₁₄, -SO₂CH₃, alkyl having
 25 1, 2, 3, 4, 5 or 6 carbon atoms, alkoxy having 1, 2, 3 or 4 carbon
 atoms or -O_x-(CH₂)_y-CF₃,
- R₁₄ is OH, alkyl having 1, 2, 3, 4, 5 or 6 carbon atoms,
 alkoxy having 1, 2, 3, 4, 5 or 6 carbon atoms
 or -O_{aa}-(CH₂)_{bb}-CF₃;
- 30 x is zero or 1;
 y is zero, 1, 2 or 3;
 aa is zero or 1;
 bb is zero, 1, 2 or 3;
- and the other of the R₃ and R₄ radicals
 35 is -O-phenyl

in which the phenyl radical is unsubstituted or substituted by 1, 2, 3, 4 or 5 radicals selected from the group consisting of F, Cl, Br, NO₂, alkyl having 1, 2, 3 or 4 carbon atoms, -SO_{qq}CH₃, -SO_{rr}CF₃, -CF₃, -OCF₃, -SF₅ and -COR₁₃;

5 qq is zero, 1 or 2,
 rr is zero, 1 or 2;

R5 is hydrogen or F;
and salts thereof;

10 Very particular preference is given to compounds of the formula I in which:

R1 is Cl, Br, I, -SO₂R6 or NO₂;

R6 is OH, F, Cl, Br, I or alkyl having 1, 2, 3 or 4 carbon atoms;

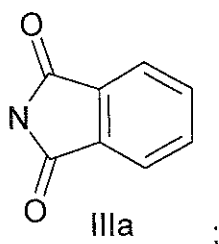
15 R2 is hydrogen, F, Cl, Br, I, -CN, -NR⁹R¹⁰, -OR¹¹, -SR¹², -COR¹³,
-(SO_r)_s-(CH₂)_t(CF₂)_u-CF₃, alkyl having 1, 2, 3, 4, 5 or 6 carbon
atoms or cycloalkyl having 3, 4, 5, 6, 7 or 8 carbon atoms, in which
1, 2, 3 or 4 hydrogen atoms may be replaced by fluorine atoms;

R9, R10, R11 and R12

20 are each independently hydrogen, alkyl having 1, 2, 3 or 4 carbon atoms, $-(CH_2)_v-(CF_2)_w-CF_3$, alkylcarbonyl having 1, 2, 3 or 4 carbon atoms or alkylsulfonyl having 1, 2, 3 or 4 carbon atoms;

or

25 R9 and R10, together with the nitrogen atom bearing them, form a heterocycle of the formula IIIa:



R13 is OH, alkyl having 1, 2, 3, 4, 5 or 6 carbon atoms or alkoxy having 1, 2, 3, 4, 5 or 6 carbon atoms;

s is zero;

30 t and u

are each independently zero or 1;

v and w

are each independently zero or 1;

one of the R3 and R4 radicals

is hydrogen, F, Cl, Br, I, -CN, -NO₂, -COR14, -SO₂CH₃, alkyl having 1, 2, 3, 4, 5 or 6 carbon atoms, alkoxy having 1, 2, 3 or 4 carbon atoms or -O_x-(CH₂)_y-CF₃,

5 R14 is OH, alkyl having 1, 2, 3, 4, 5 or 6 carbon atoms, alkoxy having 1, 2, 3, 4, 5 or 6 carbon atoms or -O_{aa}-(CH₂)_{bb}-CF₃;

 x is zero or 1;

 y is zero, 1, 2 or 3;

10 aa is zero or 1;

 bb is zero, 1, 2 or 3;

and the other of the R3 and R4 radicals

is -O-phenyl

15 in which the phenyl radical is unsubstituted or substituted by 1, 2, 3 or 4 radicals selected from the group consisting of F, Cl, Br, NO₂, alkyl having 1, 2, 3 or 4 carbon atoms, -SO₂CH₃, -SO₂CF₃, -CF₃, -OCF₃ -SF₅ and COR13;

R5 is hydrogen or F;

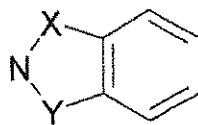
and the salts thereof.

20

In one embodiment, preference is given to compounds of the formula I in which R1 is described by Cl, Br, I, -SO₂R6 where R6 is OH, F, Cl, Br, I or alkyl having 1, 2, 3 or 4 carbon atoms, or -NO₂; particular preference is given to compounds of the formula in which R1 is described by -SO₂R6
25 where R6 is methyl or Cl, or -NO₂.

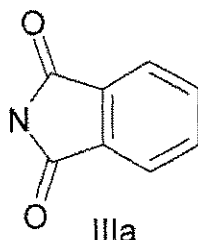
In a further embodiment, preference is given to compounds of the formula I in which R2 is described by hydrogen, F, Cl, Br, I, -CN, -(SO_r)_s-(CH₂)_t-(CF₂)_u-CF₃ where s is zero and t and u are each
30 independently zero or 1, or by -NR9R10, -OR11, -SR12, -COR13, alkyl having 1, 2, 3, 4, 5 or 6 carbon atoms, cycloalkyl having 3, 4, 5, 6, 7 or 8 carbon atoms, in which 1, 2, 3 or 4 hydrogen atoms may be replaced by fluorine atoms, where R9, R10, R11, R12 are each independently hydrogen, alkyl having 1, 2, 3 or 4 carbon atoms, -(CH₂)_v-(CF₂)_w-CF₃,
35 alkylcarbonyl having 1, 2, 3 or 4 carbon atoms or alkylsulfonyl having 1, 2, 3 or 4 carbon atoms, where v and w are each independently zero or 1, and where R13 is OH, alkyl having 1, 2, 3, 4, 5 or 6 carbon atoms or alkoxy having 1, 2, 3, 4, 5 or 6 carbon atoms, or R9 and R10, together with the

nitrogen atom which bears them, form a heterocycle of the formula III:



III

- where X and Y are each independently described by CO or SO₂; particular preference is given to compounds in which R₂ is described by hydrogen,
- 5 NR₉R₁₀ and COR₁₃, where R₉ and R₁₀ are each independently hydrogen, or alkylcarbonyl having 1, 2, 3 or 4 carbon atoms, in particular methylcarbonyl, or R₉ and R₁₀, together with the nitrogen atom which bears them, form a heterocycle of the formula III,
- where X and Y are each independently described by CO or SO₂;
- 10 in particular, R₉ and R₁₀, together with the nitrogen atom which bears them, may form a heterocycle of the formula IIIa:



IIIa

- and where R₁₃ is alkoxy having 1, 2, 3, 4, 5 or 6 carbon atoms, in particular methoxy.
- 15 In a further embodiment, R₂ in the compounds of the formula I is described by hydrogen or Br, in particular hydrogen.

- In a further embodiment, preference is given to compounds of the formula I in which one of the R₃ and R₄ radicals is described by hydrogen, F, Cl, Br, I, -CN or -COR₁₄ where R₁₄ is OH or alkoxy having 1, 2, 3, 4, 5 or 6 carbon atoms, in particular methoxy; particular preference is given to
- 20 compounds of the formula I in which one of the R₃ and R₄ radicals is described by hydrogen or Br. The particular other R₃ or R₄ radical is preferably described by -O_{ss}-phenyl where the phenyl radical is unsubstituted or substituted by 1, 2, 3, 4 or 5 radicals selected from the
- 25 group consisting of F, Cl, Br, NO₂, alkyl having 1, 2, 3 or 4 carbon atoms, -SO_{qq}CH₃, -SO_{rr}CF₃, -CF₃, -OCF₃, -SF₅, -COR₁₃ where R₁₃ is OH, alkyl having 1, 2, 3, 4, 5 or 6 carbon atoms or alkoxy having 1, 2, 3, 4, 5 or 6 carbon atoms, and where qq and rr are each independently zero, 1 or 2

and ss is zero or 1, in particular 1; particular preference is given to compounds of the formula I in which the respective other R3 or R4 radical is described by -O-phenyl where the phenyl radical is substituted by 1, 2, 3 or 4 radicals, preferably 3 or 4 radicals, selected from the group consisting of F, Cl, Br, NO₂, alkyl having 1, 2, 3 or 4 carbon atoms, -SO₂CH₃,
 5 -SO₂CF₃, -CF₃, -OCF₃, -SF₅, -COR₁₃ where R₁₃ is OH, alkyl having 1, 2, 3, 4, 5 or 6 carbon atoms or alkoxy having 1, 2, 3, 4, 5 or 6 carbon atoms, preferably selected from the group consisting of Br, NO₂, alkyl having 1, 2, 3 or 4 carbon atoms, in particular methyl, -SO₂CH₃, -COR₁₃ where R₁₃ is
 10 OH or alkoxy having 1, 2, 3, 4, 5 or 6 carbon atoms, in particular methoxy.

In a further embodiment, preference is given to compounds of the formula I in which R₅ is described by hydrogen or F; particular preference is given to compounds of the formula I in which R₅ is described by hydrogen.

15

Radicals which occur more than once, for example R₁₃, may be the same or different and each independently have the definitions specified.

When the substituents R₁ to R₅ contain one or more centers of asymmetry,
 20 they may each independently have either the S or the R configuration. The compounds may be in the form of optical isomers, of diastereomers, of racemates or of mixtures thereof in all ratios.

The disclosure herein encompasses all tautomeric forms of the compounds
 25 of the formula I.

Alkyl radicals may be straight-chain or branched. This also applies if they bear substituents or occur as substituents of other radicals, for example in fluoroalkyl radicals or alkoxy radicals. Examples of alkyl radicals are
 30 methyl, ethyl, n-propyl, isopropyl (= 1-methylethyl), n-butyl, isobutyl (= 2-methylpropyl), sec-butyl (= 1-methylpropyl), tert-butyl (= 1,1-dimethylethyl), n-pentyl, isopentyl, tert-pentyl, neopentyl and hexyl. Preferred alkyl radicals are methyl, ethyl, n-propyl and isopropyl. One or more, for example 1, 2, 3, 4 or 5, hydrogen atoms in alkyl radicals may be
 35 replaced by fluorine atoms. Examples of such fluoroalkyl radicals are trifluoromethyl, 2,2,2-trifluoroethyl and pentafluoroethyl. Substituted alkyl radicals may be substituted in any positions.

Examples of cycloalkyl radicals are cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl or cyclooctyl. In cycloalkyl radicals, one or more, for example 1, 2, 3 or 4, hydrogen atoms may be replaced by fluorine atoms. Substituted cycloalkyl radicals may be substituted in any positions. Phenyl radicals may be unsubstituted or be mono- or polysubstituted, for example mono-, di- or trisubstituted, by identical or different radicals. When a phenyl radical is substituted, it preferably has one or two identical or different substituents. This likewise applies to substituted phenyl radicals in groups such as, for example, phenylalkyl or phenyloxy. In monosubstituted phenyl radicals, the substituent may be in the 2-position, 3-position or 4-position. Disubstituted phenyl may be substituted in the 2,3-position, 2,4-position, 2,5-position, 2,6-position, 3,4-position or 3,5-position. The substituents in trisubstituted phenyl radicals may be in the 2,3,4-position, 2,3,5-position, 2,4,5-position, 2,4,6-position, 2,3,6-position or 3,4,5-position.

Heteroaryl radicals are aromatic ring compounds in which one or more ring atoms are oxygen atoms, sulfur atoms or nitrogen atoms, for example 1, 2 or 3 nitrogen atoms, 1 or 2 oxygen atoms, 1 or 2 sulfur atoms or a combination of different heteroatoms. The heteroaryl radicals may be attached via all positions, for example via the 1-position, 2-position, 3-position, 4-position, 5-position, 6-position, 7-position or 8-position. Heteroaryl radicals may be unsubstituted or be mono- or polysubstituted, for example mono-, di- or trisubstituted, by identical or different radicals. This applies likewise to heteroaryl radicals, for example in the heteroarylalkyl radical. Examples of heteroaryl are furanyl, thienyl, pyrrolyl, imidazolyl, pyrazolyl, triazolyl, tetrazolyl, oxazolyl, isoxazolyl, thiazolyl, isothiazolyl, pyridyl, pyrazinyl, pyrimidinyl, pyridazinyl, indolyl, indazolyl, quinolyl, isoquinolyl, phthalazinyl, quinoxalinyl, quinazolinyl and cinnolinyl. Heteroaryl radicals are in particular 2- or 3-thienyl, 2- or 3-furyl, 1-, 2- or 3-pyrrolyl, 1-, 2-, 4- or 5-imidazolyl, 1-, 3-, 4- or 5-pyrazolyl, 1,2,3-triazol-1-, -4- or -5-yl, 1,2,4-triazol-1-, -3- or -5-yl, 1- or 5-tetrazolyl, 2-, 4- or 5-oxazolyl, 3-, 4- or 5-isoxazolyl, 1,2,3-oxadiazol-4- or -5-yl, 1,2,4-oxadiazol-3- or -5-yl, 1,3,4-oxadiazol-2-yl or -5-yl, 2-, 4- or 5-thiazolyl, 3-, 4- or 5-isothiazolyl, 1,3,4-thiadiazol-2- or -5-yl, 1,2,4-thiadiazol-3- or -5-yl, 1,2,3-thiadiazol-4- or -5-yl, 2-, 3- or 4-pyridyl, 2-, 4-, 5- or 6-pyrimidinyl, 3- or 4-pyridazinyl, 2- or 3-pyrazinyl, 1-, 2-, 3-, 4-, 5-, 6- or 7-indolyl, 1-, 2-, 4- or 5-benzimidazolyl, 1-, 3-, 4-, 5-, 6- or 7-indazolyl, 2-, 3-, 4-, 5-, 6-, 7- or 8-quinolyl, 1-, 3-, 4-, 5-, 6-, 7- or 8-isoquinolyl, 2-, 4-, 5-, 6-,

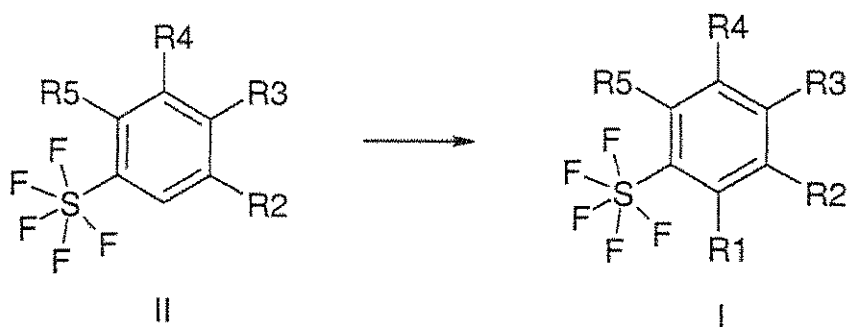
7- or 8-quinazoliny, 3-, 4-, 5-, 6-, 7- or 8-cinnoliny, 2-, 3-, 5-, 6-, 7- or 8-quinoxaliny, 1-, 4-, 5-, 6-, 7- or 8-phthalaziny. Also included are the corresponding N-oxides of these compounds, for example 1-oxy-2-, -3- or -4-pyridyl.

5

Particularly preferred heteroaromatic radicals are 2- or 3-thienyl, 2- or 3-furyl, 1-, 2- or 3-pyrrolyl, 1-, 2-, 4- or 5-imidazolyl, 2-, 3-, 4-, 5-, 6-, 7- or 8-quinolyl, 1-, 3-, 4- or 5-pyrazolyl, 2-, 3- or 4-pyridyl, 2- or 3-pyrazinyl, 2-, 4-, 5- or 6-pyrimidinyl and 3- or 4-pyridazinyl.

10

In a second aspect, there is provided a process for preparing the compounds of the formula I or the salts thereof, which comprises converting compounds of the formula II by electrophilic aromatic substitution to compounds of the formula I



15

where R1 to R5 are each as defined above.

In a third aspect, there is provided a compound of the formula I and/or salts thereof as defined above for use as a synthetic intermediate.

20

In a fourth aspect, there is provided a compound of the formula I and/or salts thereof as defined above for use as a synthetic intermediate for the preparation of medicaments, diagnostic aids, liquid crystals, polymers, pesticides, herbicides, fungicides, nematocides, parasiticides, insecticides, acaricides and arthropodocides.

25

In the preparation of the compounds of the formula I, the procedure is to carry out an electrophilic aromatic substitution, preferably a halogenation, chlorosulfonation or nitration.

30

In one embodiment, halogenation (R1 = Cl, Br or I) is effected as described in R.C. Larock, Comprehensive Organic Transformations: A Guide to Functional Group Preparations, VCH Publishers, New York, Weinheim,

1999, pages 619-628 and in the literature cited therein. The chlorination is effected, for example, with NCIS in an inert solvent, for example isopropanol, CHCl_3 , CH_2Cl_2 or EA at a temperature between -30°C and 100°C , preferably between 40°C and the boiling point of the solvent. The

- 5 bromination is effected, for example using NBS in an acid preferably in a mixture comprising trifluoroacetic acid and sulfuric acid at a temperature between -20°C and 80°C , preferably between 0°C and 40°C .

In another embodiment, sulfonation or chlorosulfonation ($\text{R1} = \text{SO}_2\text{R6}$ where R6 is OH or Cl) is effected as described in March's Advanced

Organic Chemistry 5th edition 2001, pages 702-703 and in the literature cited therein.

In another embodiment, nitration ($R1 = NO_2$) is effected as described, for example, in Houben-Weyl, Methoden der organischen Chemie, 4th edition, 5
Organo-Stickstoff-Verbindungen IV, part 1, Georg Thieme Verlag Stuttgart 1992, pages 262-341 and in the literature cited therein. Compounds of the formula II where $R4 = \text{phenyl}$ in which the phenyl may be substituted as described under $R3$ are nitrated, for example, with a 90% aqueous HNO_3 solution at a temperature between $-80^\circ C$ and $20^\circ C$, preferably 10
between $-60^\circ C$ and $-20^\circ C$.

From the compounds of the formula I where $R1 = NO_2$, it is possible to prepare the corresponding anilines ($R1 = NH_2$) as described in 15
R.C. Larock, Comprehensive Organic Transformations: A Guide to Functional Group Preparations, VCH Publishers, New York, Weinheim, 1999, 821-828 and the literature cited therein. From these anilines, it is possible to synthesize, via the diazonium salts by methods known to those skilled in the art, as described, for example, in Houben-Weyl, Methoden der organischen Chemie, 4th edition, Organo-Stickstoff-Verbindungen I, part 2, 20
Georg Thieme Verlag Stuttgart 1990, pages 1060-1136 and in the references cited therein, the compounds of the formula I with further definitions of $R1$.

The starting compounds of the formulae II are commercially available or 25
can be prepared by processes similar to those described in the literature and/or known to those skilled in the art.

In the starting compounds, functional groups may also be present in protected form or in the form of precursors, and then be converted to the 30
desired groups in the compounds of the formula I prepared by the process described above. Appropriate protecting group techniques are known to those skilled in the art.

The workup and, if desired, the purification of the products and/or 35
intermediates is effected by conventional methods such as extraction, chromatography or crystallization and conventional dryings.

Also claimed are the compounds of the formula I and/or the salts thereof for

use as a synthetic intermediate, in particular for use as a synthetic intermediate for preparing medicaments, diagnostic aids, liquid crystals, polymers, pesticides, herbicides, fungicides, nematocides, parasiticides, insecticides, acaricides and arthropodocides.

5

Examples of the various possible uses of pentafluorosulfanyl derivatives are described in the following publications: WO 9421606, WO 03093228 A1 (insecticides, acaricides); DE 19711953, GB 2276379 (herbicides); DE 10124480, DE 10353658, Angew. Chem. 1999, 111, 2174, Angew. Chem. 2000, 112, 4384 (liquid crystals); WO 03097591 (medicaments, diagnostic aids); US 5220070, US 5302692 (polymers); WO 03093228, WO 9625401 (pesticides); GB 2276381, GB 2276380 (fungicides), US 5637607 (nematocides), WO 9947139 (parasiticides), US 6531501, WO 9516676 (arthropodocides).

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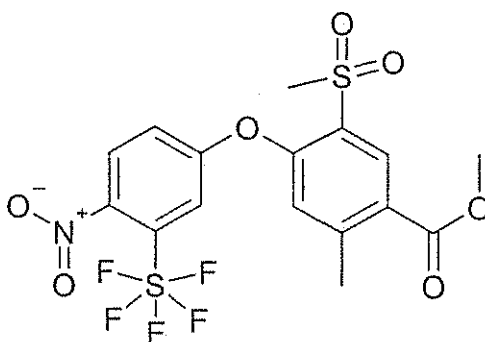
The compounds of the formula I can be isolated in the form of their salts. These are obtained by the conventional methods by reaction with acids or bases. Useful acid addition salts are, for example, halides, especially hydrochlorides, hydrobromides, lactates, sulfates, citrates, tartrates, acetates, phosphates, methylsulfonates, benzenesulfonates, p-toluenesulfonates, adipates, fumarates, gluconates, glutamates, glycerolphosphates, maleates, benzoates, oxalates and pamoates and trifluoroacetates, and in the case of the preparation of active ingredients preferably pharmaceutically acceptable salts. If the compounds contain an acidic group, they can form salts with bases, for example alkali metal salts, preferably sodium or potassium salts, or ammonium salts, for example as salts with ammonia or organic amines or amino acids. They may also be in the form of a zwitterion.

30 List of abbreviations:

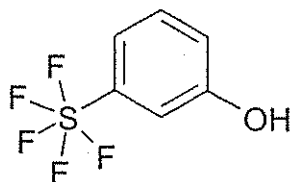
DIP	diisopropyl ether
DIPEA	diisopropylethylamine
DME	1,2-dimethoxyethane
DMF	N,N-dimethylformamide
35 EA	ethyl acetate
eq.	equivalent
HEP	n-heptane
HOAc	acetic acid

MeOH	methanol
mp	melting point
MTB	tert-butyl methyl ether
NBS	2-bromoisindole-1,3-dione
5 NCIS	2-chloroisindole-1,3-dione
RT	room temperature
THF	tetrahydrofuran

Example 1: Methyl 5-methanesulfonyl-2-methyl-4-(4-nitro-3-pentafluoro-sulfanylphenoxy)benzoate



a) 3-Pentafluorosulfanylphenol



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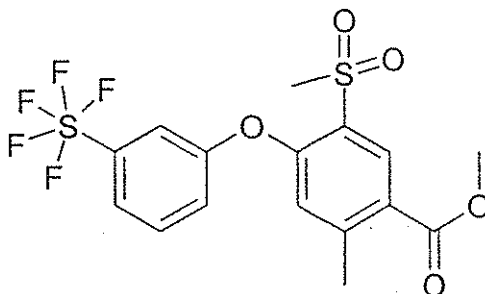
5.0 g of 3-pentafluorosulfanylaniline (Tetrahedron 56, (2000) 3399) were suspended in 50 ml of a 35% aqueous H_2SO_4 solution. At 0°C , a solution of 1.57 g of NaNO_2 in 5 ml of water was then added dropwise within 10 minutes. The mixture was stirred at 0°C for a further 40 minutes. A solution, cooled to 0°C , of 8.56 g of $\text{Cu}(\text{NO}_3)_2$ in 50 ml of water was then added to this suspension. Directly thereafter, 3.26 g of Cu_2O were also added, and distinct gas evolution could be observed. The mixture was extracted 3 times with 100 ml each time of CH_2Cl_2 , the organic phase was washed with 100 ml of a saturated aqueous NaCl solution and dried over MgSO_4 , and the solvent was removed under reduced pressure. Chromatography on silica gel with DIP afforded 3.5 g of the phenol as a colorless oil.

25

R_f (EE/HEP 1:10) = 0.15

MS (EI) : 220

b) Methyl 5-methanesulfonyl-2-methyl-4-(3-pentafluorosulfanylphenoxy)-benzoate



5

5.00 g of 3-pentafluorosulfanylphenol, 6.98 g of methyl 4-bromo-5-methanesulfonyl-2-methylbenzoate (Journal of Medicinal Chemistry (1997), 40(13), 2017) and 22.20 g of Cs_2CO_3 were stirred in 200 ml of anhydrous DMF at 100°C for 2 h. The mixture was allowed to cool, and the reaction mixture was poured onto 1 l of water and stirred at RT for 16 h. The product was then filtered off and dried under reduced pressure. 8.20 g of pale yellow crystals were obtained, mp 139°C (with decomposition).

R_f (DIP) = 0.27

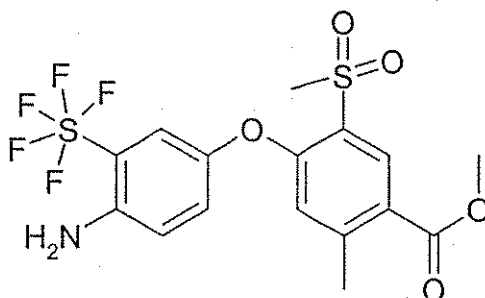
MS (ES^+): 446

15 c) Methyl 5-methanesulfonyl-4-(4-nitro-3-pentafluorosulfanylphenoxy)-2-methylbenzoate

3.50 g of methyl 5-methanesulfonyl-2-methyl-4-(3-pentafluorosulfanylphenoxy)benzoate were dissolved at -40°C in 100 ml of 90% HNO_3 . The mixture was stirred at this temperature for 10 minutes and then the mixture was poured onto 800 g of ice. This mixture was stirred for 10 minutes and the product was subsequently filtered off with suction. 3.89 g of a pale yellow solid were obtained, mp $145\text{--}148^\circ\text{C}$ (with decomposition).

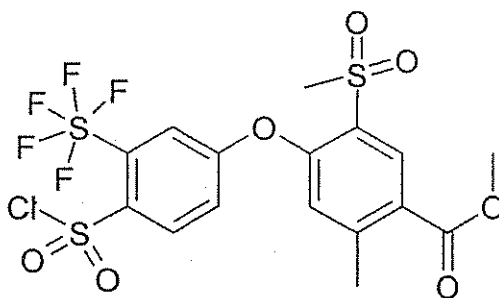
R_f (DIP) = 0.09

25 Example 2: Methyl 4-(4-amino-3-pentafluorosulfanylphenoxy)-5-methanesulfonyl-2-methylbenzoate



3.80 g of methyl 5-methanesulfonyl-4-(4-nitro-3-pentafluorosulfanylphenoxy)-2-methylbenzoate (example 1) were dissolved in 30 ml of HOAc and 30 ml of MeOH, admixed with 200 mg of Pd/C (10%) and hydrogenated under 6 bar of hydrogen pressure for 24 h. Since the reaction was not yet complete, a further 300 mg of Pd/C (10%), 30 ml of HOAc and 30 ml of MeOH were added and the mixture was hydrogenated under 6 bar of hydrogen pressure for a further 24 h. Subsequently, the catalyst was filtered off and the solvents were removed under reduced pressure. 3.4 g of a light gray solid were obtained, mp 175°C (with decomposition).
Rf (MTB) = 0.44

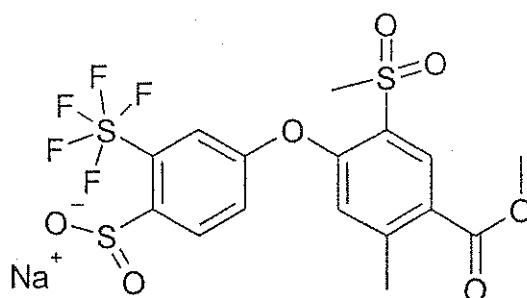
Example 3: Methyl 4-(4-chlorosulfonyl-3-pentafluorosulfanylphenoxy)-5-methanesulfonyl-2-methylbenzoate



3.4 g of methyl 4-(4-amino-3-pentafluorosulfanylphenoxy)-5-methanesulfonyl-2-methylbenzoate (example 2) were dissolved in 30 ml of HOAc, and admixed with 30 g of ice and subsequently with 30 ml of a saturated aqueous HCl solution. A solution of 0.56 g of NaNO₂ in 5 ml of water was added dropwise at 0°C to this solution within 5 minutes. The mixture was stirred at 0°C for 10 minutes. This solution was then added in portions to a suspension, at 0°C, of 12.4 mg of CuCl and 125.6 mg of CuCl₂ (dihydrate) in 100 ml of SO₂-saturated acetic acid. The mixture was stirred at RT for 2 h, then diluted with 300 ml of water and extracted 3 times with 200 ml each time of EA. The mixture was dried over MgSO₄ and the solvent was removed under reduced pressure. 3.5 g of a viscous oil were obtained and were reacted further without purification.

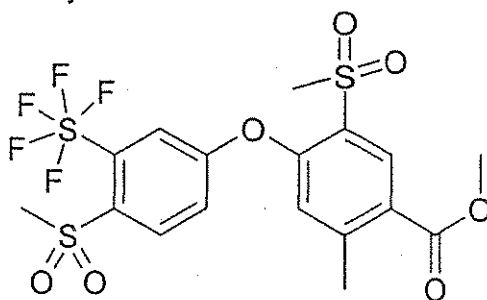
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Example 4: Sodium 4-(2-methanesulfonyl-4-methoxycarbonyl-5-methylphenoxy)-2-pentafluorosulfanylbenzenesulfinate

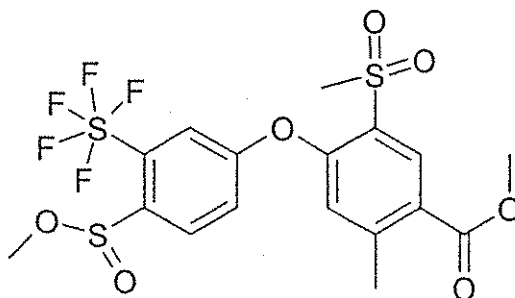


- 3.5 g of methyl 4-(4-chlorosulfonyl-3-pentafluorosulfanylphenoxy)-5-methanesulfonyl-2-methylbenzoate (example 3) were added in portions to a solution, at 70°C, of 8.10 g of Na₂SO₃ in 75 ml of water and kept at about pH = 10 with 10 molar aqueous NaOH solution. Subsequently, the mixture was stirred at 70°C for 45 minutes, then allowed to cool and adjusted to pH = 2 with aqueous HCl solution. The mixture was extracted 3 times with 200 ml each time of EA. The mixture was dried over MgSO₄ and the solvent was removed under reduced pressure. The residue was suspended in 100 ml of water and adjusted to pH = 10 with a 2 molar aqueous NaOH solution, and the volatile constituents were removed under reduced pressure. The mixture was subsequently extracted twice with 100 ml each time of toluene and then coevaporated with 100 ml of anhydrous DMF, and the residue (3.0 g) was reacted further without purification.

Example 5: Methyl 5-methanesulfonyl-4-(4-methanesulfonyl-3-pentafluorosulfanylphenoxy)-2-methylbenzoate



- and methyl 5-methanesulfonyl-4-(4-methoxysulfinyl-3-pentafluorosulfanylphenoxy)-2-methylbenzoate

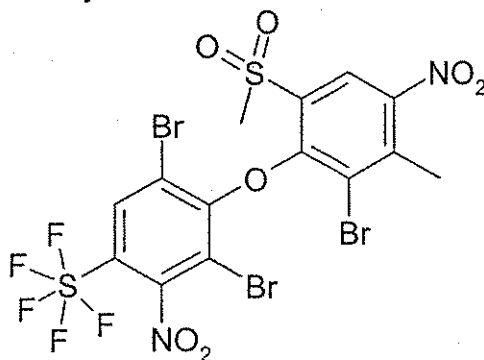


3.0 g of sodium 4-(2-methanesulfonyl-4-methoxycarbonyl-5-methylphenoxy)-2-pentafluorosulfanylbzenesulfinate (example 4) were dissolved in 100 ml of anhydrous DMF, 4.0 g of CH_3I were added and the mixture was stirred at 45°C for 9 h. The reaction mixture was subsequently left to stand at RT for 2 days. The solvent was then removed under reduced pressure and the residue taken up with 100 ml of water and 100 ml of EA. 50 ml of a 5% aqueous NaHSO_4 solution were then added and the phases were separated. Subsequently, the mixture was extracted 3 times with 100 ml each time of EA. The mixture was dried over MgSO_4 , the solvent was removed under reduced pressure and the residue was chromatographed on silica gel with 1:1 MTB/DIP. 0.59 g of methyl 5-methanesulfonyl-4-(4-methanesulfonyl-3-pentafluorosulfanylphenoxy)-2-methylbenzoate and 0.49 g of methyl 5-methanesulfonyl-4-(4-methoxysulfinyl-3-pentafluorosulfanylphenoxy)-2-methylbenzoate were obtained.

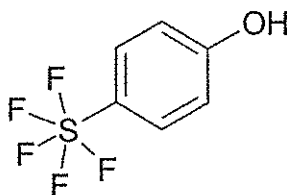
R_f (MTB/DIP 1:1) = 0.13: methyl 5-methanesulfonyl-4-(4-methanesulfonyl-3-pentafluorosulfanylphenoxy)-2-methylbenzoate

R_f (MTB/DIP 1:1) = 0.32: methyl 5-methanesulfonyl-4-(4-methoxysulfinyl-3-pentafluorosulfanylphenoxy)-2-methylbenzoate

Example 6: 3-Bromo-4-(2,6-dibromo-3-nitro-4-pentafluorosulfanylphenoxy)-5-methanesulfonyl-2-methylnitrobenzene



a) 4-Pentafluorosulfanylphenol

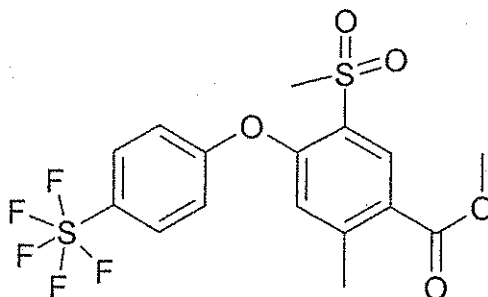


40.00 g of 4-pentafluorosulfanylaniline (Tetrahedron 56, (2000) 3399) were suspended in 500 ml of a 35% aqueous H_2SO_4 solution. At 0°C , a solution of 13.85 g of NaNO_2 in 30 ml of water was then added dropwise within 10 minutes. The mixture was stirred at 0°C for a further 35 minutes. A solution, cooled to 0°C , of 171.10 g of $\text{Cu}(\text{NO}_3)_2$ in 200 ml of water was then added to this suspension. Directly thereafter, 26.11 g of Cu_2O were also added, and distinct gas evolution could be observed. The mixture was stirred at RT for a further 2 hours, then the mixture was extracted 3 times with 200 ml each time of CH_2Cl_2 , the combined organic phases were dried over MgSO_4 and the solvent was removed under reduced pressure. Chromatography on silica gel with DIP afforded 3.5 g of the phenol as a colorless oil.

Rf (EA/HEP 1:10) = 0.15

MS (EI) : 220

b) Methyl 5-methanesulfonyl-2-methyl-4-(4-pentafluorosulfanylphenoxy)-benzoate

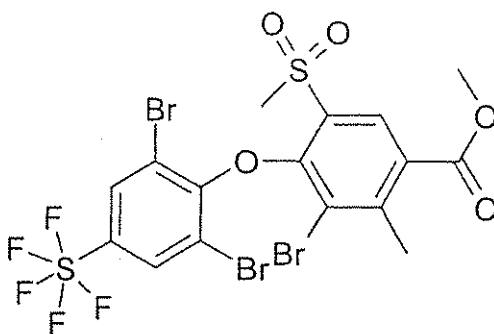


5.00 g of 4-pentafluorosulfanylphenol, 6.98 g of methyl 4-bromo-5-methanesulfonyl-2-methylbenzoate (Journal of Medicinal Chemistry (1997), 40(13), 2017) and 22.20 g of Cs_2CO_3 were stirred in 200 ml of anhydrous DMF at 100°C for 2 h. The reaction mixture was allowed to cool and poured onto 1 l of water, and the solid was filtered off with suction and dried. 8.00 g of an amorphous solid were obtained.

Rf (EA/HEP 1:10) = 0.26

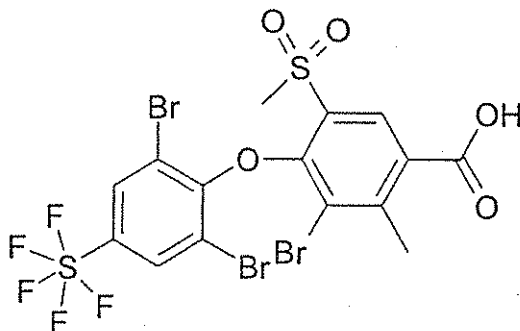
MS (ES+) : 446

c) Methyl 3-bromo-4-(2,6-dibromo-4-pentafluorosulfanylphenoxy)-5-methanesulfonyl-2-methylbenzoate



- 8.00 g of methyl 5-methanesulfonyl-2-methyl-4-(4-pentafluorosulfanylphenoxy)benzoate were dissolved in 200 ml of trifluoroacetic acid and 20 ml of 97% H_2SO_4 were added. At RT, 9.57 g of NBS were then added in 3 portions. The mixture was stirred at RT for 2 hours, then a further 4.00 g of NBS were added in two portions. The mixture was then left to stand at RT for 16 hours, then poured onto 300 g of ice and adjusted to $\text{pH} > 7$ with saturated aqueous Na_2CO_3 solution. 5.00 g of Na_2SO_3 were then added and the mixture was extracted 3 times with 500 ml each time of EA. The mixture was washed 3 times with semisaturated aqueous Na_2CO_3 solution, then dried over MgSO_4 , and the solvent was removed under reduced pressure. 6.4 g of an amorphous solid were obtained.
- R_f (DIP) = 0.48

- d) 3-Bromo-4-(2,6-dibromo-4-pentafluorosulfanylphenoxy)-5-methanesulfonyl-2-methylbenzoic acid



- 6.2 g of methyl 3-bromo-4-(2,6-dibromo-4-pentafluorosulfanylphenoxy)-5-methanesulfonyl-2-methylbenzoate were dissolved in 300 ml of MeOH, and 100 ml of water and also 5.45 ml of a 2 molar aqueous NaOH solution were added. The mixture was stirred at RT for 20 hours, then heated to reflux for 3 hours. The MeOH was removed under reduced pressure, diluted with 200 ml of water and adjusted to $\text{pH} < 2$ with an aqueous HCl solution. The mixture was stirred at RT for a further 10 minutes and then the product was filtered off with suction. 6.0 g of a colorless solid were obtained, mp 228°C (with decomposition).

R_f (DIP 2%HOAc) = 0.15

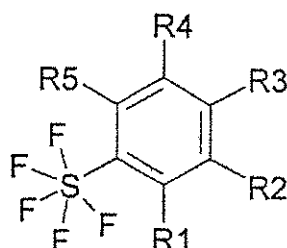
MS (ES^-): 666

e) 3-Bromo-4-(2,6-dibromo-3-nitro-4-pentafluorosulfanylphenoxy)-5-methanesulfonyl-2-methylnitrobenzene

- 5 200 mg of 3-bromo-4-(2,6-dibromo-4-pentafluorosulfanylphenoxy)-5-methanesulfonyl-2-methylbenzoic acid were stirred in 500 μ l of a 90% aqueous HNO_3 solution and 50 μ l of 97% H_2SO_4 at RT for one hour. The mixture was then poured onto 50 ml of water, and the product filtered off with suction and dried under reduced pressure. 200 mg of an amorphous
- 10 solid were obtained. MS (ES^-): 711

What is claimed is:

1. A compound of the formula I



I

5 where

R1 is Cl, Br, I, -CN, -SO₂R₆, NO₂, alkoxy having 1, 2, 3 or 4 carbon atoms, NR₇R₈, -O-(CH₂)_b-(CF₂)_c-CF₃, -(SO_d)_e-(CH₂)_f-(CF₂)_g-CF₃, alkyl having 1, 2, 3, 4, 5 or 6 carbon atoms or cycloalkyl having 3, 4, 5, 6, 7 or 8 carbon atoms, in which 1, 2, 3 or 4 hydrogen atoms may be replaced by fluorine atoms;

R₆ is OH, F, Cl, Br, I or alkyl having 1, 2, 3 or 4 carbon atoms;

R₇ and R₈

are each independently hydrogen, alkyl having 1, 2, 3 or 4 carbon atoms or -CH₂-CF₃;

b and c

are each independently zero or 1;

d is zero, 1 or 2;

e is zero or 1;

f is zero, 1, 2, 3 or 4;

g is zero or 1;

or

R1 is -(CH₂)_h-phenyl or -O-phenyl,

in which the phenyl radicals are unsubstituted or substituted by 1, 2 or 3 radicals selected from the group consisting of F, Cl, Br, I, -O_j-(CH₂)_k-CF₃, alkoxy having 1, 2, 3 or 4 carbon atoms, alkyl having 1, 2, 3 or 4 carbon atoms and -SO₂CH₃;

j is zero or 1;

k is zero, 1, 2 or 3;

h is zero, 1, 2, 3 or 4;

or

R1 is $-(CH_2)_l$ -heteroaryl

which is unsubstituted or substituted by 1, 2 or 3 radicals selected from the group consisting of F, Cl, Br, I, $-O_m-(CH_2)_n-CF_3$, alkoxy having 1, 2, 3 or 4 carbon atoms, alkyl having 1, 2, 3 or 4 carbon atoms and $-SO_2CH_3$;

m is zero or 1;

n is zero, 1, 2 or 3;

l is zero, 1, 2, 3 or 4;

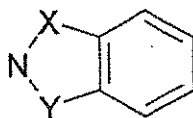
R2 is hydrogen, F, Cl, Br, I, $-CN$, NR_9R_{10} , $-OR_{11}$, $-SR_{12}$, $-COR_{13}$, $-SO_qCH_3$, $-(SO_r)_s-(CH_2)_t-(CF_2)_u-CF_3$, alkyl having 1, 2, 3, 4, 5 or 6 carbon atoms or cycloalkyl having 3, 4, 5, 6, 7 or 8 carbon atoms, in which 1, 2, 3 or 4 hydrogen atoms may be replaced by fluorine atoms;

R_9 , R_{10} , R_{11} and R_{12}

are each independently hydrogen, alkyl having 1, 2, 3 or 4 carbon atoms, $-(CH_2)_v-(CF_2)_w-CF_3$, alkylcarbonyl having 1, 2, 3 or 4 carbon atoms or alkylsulfonyl having 1, 2, 3 or 4 carbon atoms;

or

R_9 and R_{10} , together with the nitrogen atom bearing them, form a heterocycle of the formula III:



III

X and Y

are each independently CO or SO_2 ;

R13 is OH, alkyl having 1, 2, 3, 4, 5 or 6 carbon atoms or alkoxy having 1, 2, 3, 4, 5 or 6 carbon atoms;

q and r

are each independently 1 or 2;

s is zero or 1;

t is zero, 1, 2, 3 or 4;

u is zero or 1;

v is zero, 1, 2, 3 or 4;

w is zero or 1;

one of the R_3 and R_4 radicals

is hydrogen, F, Cl, Br, I, -CN, -NO₂, -COR₁₄, -SO₂CH₃, alkyl having 1, 2, 3, 4, 5 or 6 carbon atoms, alkoxy having 1, 2, 3 or 4 carbon atoms, -O_x-(CH₂)_y-CF₃,

5 R₁₄ is OH, alkyl having 1, 2, 3, 4, 5 or 6 carbon atoms, alkoxy having 1, 2, 3, 4, 5 or 6 carbon atoms or -O_{aa}-(CH₂)_{bb}-CF₃;

x is zero or 1;

y is zero, 1, 2 or 3;

aa is zero or 1;

10 bb is zero, 1, 2 or 3;

and the other of the R₃ and R₄ radicals

is O_{ss}-phenyl,

in which the phenyl radical is unsubstituted or substituted by 1, 2, 3, 4 or 5 radicals selected from the group consisting of F, Cl, Br, I, NO₂, alkyl having 1, 2, 3 or 4 carbon atoms, -SO_{qq}CH₃, -SO_{rr}CF₃, -CF₃, -OCF₃, -SF₅, -CN or -COR₁₃;

qq is zero, 1 or 2;

rr is zero, 1 or 2,

ss is zero or 1;

20 R₅ is hydrogen, -NO₂, -SO₂Cl, F, Cl, Br, I, -CN, -SO₂CH₃, alkoxy having 1, 2, 3 or 4 carbon atoms, NR₁₅R₁₆, -O-(CH₂)_{ee}-(CF₂)_{ff}-CF₃, -(SO_{gg})_{hh}-(CH₂)_{jj}-(CF₂)_{kk}-CF₃, alkyl having 1, 2, 3, 4, 5 or 6 carbon atoms or cycloalkyl having 3, 4, 5, 6, 7 or 8 carbon atoms in which 1, 2, 3 or 4 hydrogen atoms may be replaced by

25 fluorine atoms;

R₁₅ and R₁₆

are each independently hydrogen, alkyl having 1, 2, 3 or 4 carbon atoms or -CH₂-CF₃;

ee and ff

30 are each independently zero or 1;

gg is zero, 1 or 2;

hh is zero or 1;

jj is zero, 1, 2, 3 or 4;

kk is zero or 1;

35 or

R₅ is -(CH₂)_{ll}-phenyl or -O-phenyl,

in which the phenyl radicals are unsubstituted or substituted by 1, 2 or 3 radicals selected from the group consisting of F, Cl, Br,

I, $-O_{mm}-(CH_2)_{nn}-CF_3$, alkoxy having 1, 2, 3 or 4 carbon atoms, alkyl having 1, 2, 3 or 4 carbon atoms and $-SO_2CH_3$;

mm is zero or 1;

nn is zero, 1, 2 or 3;

5 ll is zero, 1, 2, 3 or 4;

or

R5 is $-(CH_2)_{oo}$ -heteroaryl

which is unsubstituted or substituted by 1, 2 or 3 radicals selected from the group consisting of F, Cl, Br, I, $-O_{pp}-(CH_2)_{rr}-CF_3$, alkoxy having 1, 2, 3 or 4 carbon atoms, alkyl having 1, 2, 3 or 4 carbon atoms and $-SO_2CH_3$;

10

pp is zero or 1;

rr is zero, 1, 2 or 3;

oo is zero, 1, 2, 3 or 4;

15 and salts thereof.

2. A compound of the formula I as claimed in claim 1, in which:

R1 is Cl, Br, I, $-CN$, $-SO_2R_6$, NO_2 , alkoxy having 1, 2, 3 or 4 carbon atoms, NR_7R_8 , $-O-(CH_2)_b-(CF_2)_c-CF_3$, $-(SO_d)_e-(CH_2)_f-(CF_2)_g-CF_3$, alkyl having 1, 2, 3, 4, 5 or 6 carbon atoms or cycloalkyl having 3, 4, 5, 6, 7 or 8 carbon atoms, in which 1, 2, 3 or 4 hydrogen atoms may be replaced by fluorine atoms;

20

R6 is OH, F, Cl, Br, I or alkyl having 1, 2, 3 or 4 carbon atoms;

25

R7 and R8

are each independently hydrogen, alkyl having 1, 2, 3 or 4 carbon atoms or $-CH_2-CF_3$;

b and c

are each independently zero or 1;

30

d is zero, 1 or 2;

e is zero or 1;

f is zero, 1, 2, 3 or 4;

g is zero or 1;

or

35 R1 is $-(CH_2)_h$ -phenyl or $-O$ -phenyl,

in which the phenyl radicals are unsubstituted or substituted by 1, 2 or 3 radicals selected from the group consisting of F, Cl, Br, I, $-O_j-(CH_2)_k-CF_3$, alkoxy having 1, 2, 3 or 4 carbon atoms, alkyl

having 1, 2, 3 or 4 carbon atoms and $-\text{SO}_2\text{CH}_3$;

j is zero or 1;

k is zero, 1, 2 or 3;

h is zero, 1, 2, 3 or 4;

5 or

R1 is $-(\text{CH}_2)_l$ -heteroaryl

which is unsubstituted or substituted by 1, 2 or 3 radicals selected from the group consisting of F, Cl, Br, I, $-\text{O}_m(\text{CH}_2)_n\text{CF}_3$, alkoxy having 1, 2, 3 or 4 carbon atoms, alkyl having 1, 2, 3 or 4 carbon atoms and $-\text{SO}_2\text{CH}_3$;

10

m is zero or 1;

n is zero, 1, 2 or 3;

l is zero, 1, 2, 3 or 4;

R2 is hydrogen, F, Cl, Br, I, $-\text{CN}$, NR_9R_{10} , $-\text{OR}_{11}$, $-\text{SR}_{12}$, $-\text{COR}_{13}$, $-\text{SO}_q\text{CH}_3$, $-(\text{SO}_r)_s-(\text{CH}_2)_t(\text{CF}_2)_u\text{CF}_3$, alkyl having 1, 2, 3, 4, 5 or 6 carbon atoms or cycloalkyl having 3, 4, 5, 6, 7 or 8 carbon atoms, in which 1, 2, 3 or 4 hydrogen atoms may be replaced by fluorine atoms;

15

R9, R10, R11 and R12

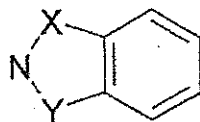
20

are each independently hydrogen, alkyl having 1, 2, 3 or 4 carbon atoms, $-(\text{CH}_2)_v(\text{CF}_2)_w\text{CF}_3$, alkylcarbonyl having 1, 2, 3 or 4 carbon atoms or alkylsulfonyl having 1, 2, 3 or 4 carbon atoms;

or

25

R9 and R10, together with the nitrogen atom bearing them, form a heterocycle of the formula III:



III

X and Y

are each independently CO or SO_2 ;

30

R13 is OH, alkyl having 1, 2, 3, 4, 5 or 6 carbon atoms or alkoxy having 1, 2, 3, 4, 5 or 6 carbon atoms;

q and r

are each independently 1 or 2;

s is zero or 1;

t is zero, 1, 2, 3 or 4;

u is zero or 1;

v is zero, 1, 2, 3 or 4;

w is zero or 1;

5 one of the R3 and R4 radicals

is hydrogen, F, Cl, Br, I, -CN, -NO₂, -COR₁₄, -SO₂CH₃, alkyl having 1, 2, 3, 4, 5 or 6 carbon atoms, alkoxy having 1, 2, 3 or 4 carbon atoms, -O_x-(CH₂)_y-CF₃,

10 R₁₄ is OH, alkyl having 1, 2, 3, 4, 5 or 6 carbon atoms, alkoxy having 1, 2, 3, 4, 5 or 6 carbon atoms or -O_{aa}-(CH₂)_{bb}-CF₃;

x is zero or 1;

y is zero, 1, 2 or 3;

aa is zero or 1;

15 bb is zero, 1, 2 or 3;

and the other of the R3 and R4 radicals

is -O-phenyl

in which the phenyl radical is unsubstituted or substituted by 1, 2, 3, 4 or 5 radicals selected from the group consisting of F, Cl, Br, I, NO₂, alkyl having 1, 2, 3 or 4 carbon atoms, -SO_{qq}CH₃, -SO_{rr}CF₃, -CF₃, -OCF₃, -SF₅, -CN or -COR₁₃;

qq is zero, 1 or 2,

rr is zero, 1 or 2;

25 R₅ is hydrogen, -NO₂, -SO₂Cl, F, Cl, Br, I, -CN, -SO₂CH₃, alkoxy having 1, 2, 3 or 4 carbon atoms, NR₁₅R₁₆, -O-(CH₂)_{ee}-(CF₂)_{ff}-CF₃, -(SO_{gg})_{hh}-(CH₂)_{jj}-(CF₂)_{kk}-CF₃, alkyl having 1, 2, 3, 4, 5 or 6 carbon atoms or cycloalkyl having 3, 4, 5, 6, 7 or 8 carbon atoms in which 1, 2, 3 or 4 hydrogen atoms may be replaced by fluorine atoms;

30 R₁₅ and R₁₆

are each independently hydrogen, alkyl having 1, 2, 3 or 4 carbon atoms or -CH₂-CF₃;

ee and ff

are each independently zero or 1;

35 gg is zero, 1 or 2;

hh is zero or 1;

jj is zero, 1, 2, 3 or 4;

kk is zero or 1;

or

R5 is $-(CH_2)_l$ -phenyl or -O-phenyl,
in which the phenyl radicals are unsubstituted or substituted by 1, 2
or 3 radicals selected from the group consisting of F, Cl, Br,
5 I, $-O_{mm}-(CH_2)_{nn}-CF_3$, alkoxy having 1, 2, 3 or 4 carbon atoms, alkyl
having 1, 2, 3 or 4 carbon atoms and $-SO_2CH_3$;

mm is zero or 1;

nn is zero, 1, 2 or 3;

ll is zero, 1, 2, 3 or 4;

10 or

R5 is $-(CH_2)_{oo}$ -heteroaryl
which is unsubstituted or substituted by 1, 2 or 3 radicals selected
from the group consisting of F, Cl, Br, I, $-O_{pp}-(CH_2)_r-CF_3$, alkoxy
having 1, 2, 3 or 4 carbon atoms, alkyl having 1, 2, 3 or 4 carbon
15 atoms and $-SO_2CH_3$;

pp is zero or 1;

rr is zero, 1, 2 or 3;

oo is zero, 1, 2, 3 or 4;

and salts thereof;

20

3. A compound of the formula I as claimed in claim 1 or 2, in which:

R1 is Cl, Br, I, -CN, $-SO_2R_6$, NO_2 , alkoxy having 1, 2, 3 or 4 carbon
atoms, NR_7R_8 , $-O-(CH_2)_b-(CF_2)_c-CF_3$, $-(SO_d)_e-(CH_2)_f-(CF_2)_g-CF_3$,
alkyl having 1, 2, 3, 4, 5 or 6 carbon atoms or cycloalkyl having 3, 4,
25 5, 6, 7 or 8 carbon atoms, in which 1, 2, 3 or 4 hydrogen atoms may
be replaced by fluorine atoms;

R6 is OH, F, Cl, Br, I or alkyl having 1, 2, 3 or 4 carbon
atoms;

R7 and R8

30

are each independently hydrogen, alkyl having 1, 2, 3
or 4 carbon atoms or $-CH_2-CF_3$;

b and c

are each independently zero or 1;

d is zero, 1 or 2;

35

e is zero or 1;

f is zero, 1, 2, 3 or 4;

g is zero or 1;

or

R1 is $-(CH_2)_h$ -phenyl or -O-phenyl,
 in which the phenyl radicals are unsubstituted or substituted by 1, 2
 or 3 radicals selected from the group consisting of F, Cl, Br,
 I, $-O_j-(CH_2)_k-CF_3$, alkoxy having 1, 2, 3 or 4 carbon atoms, alkyl
 having 1, 2, 3 or 4 carbon atoms and $-SO_2CH_3$;

j is zero or 1;
 k is zero, 1, 2 or 3;
 h is zero, 1, 2, 3 or 4;

or

10 R1 is $-(CH_2)_l$ -heteroaryl
 which is unsubstituted or substituted by 1, 2 or 3 radicals selected
 from the group consisting of F, Cl, Br, I, $-O_m-(CH_2)_n-CF_3$, alkoxy
 having 1, 2, 3 or 4 carbon atoms, alkyl having 1, 2, 3 or 4 carbon
 atoms and $-SO_2CH_3$;

15 m is zero or 1;
 n is zero, 1, 2 or 3;
 l is zero, 1, 2, 3 or 4;

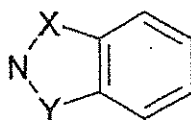
20 R2 is hydrogen, F, Cl, Br, I, -CN, -NR₉R₁₀, -OR₁₁, -SR₁₂, -COR₁₃,
 $-(SO_r)_s-(CH_2)_t-(CF_2)_u-CF_3$, alkyl having 1, 2, 3, 4, 5 or 6 carbon
 atoms or cycloalkyl having 3, 4, 5, 6, 7 or 8 carbon atoms, in which
 1, 2, 3 or 4 hydrogen atoms may be replaced by fluorine atoms;

R₉, R₁₀, R₁₁ and R₁₂

25 are each independently hydrogen, alkyl having 1, 2, 3
 or 4 carbon atoms, $-(CH_2)_v-(CF_2)_w-CF_3$, alkylcarbonyl
 having 1, 2, 3 or 4 carbon atoms or alkylsulfonyl having
 1, 2, 3 or 4 carbon atoms;

or

R₉ and R₁₀, together with the nitrogen atom bearing them,
 form a heterocycle of the formula III:



III

30

X and Y

are each independently CO or SO₂;

R₁₃ is OH, alkyl having 1, 2, 3, 4, 5 or 6 carbon atoms or
 alkoxy having 1, 2, 3, 4, 5 or 6 carbon atoms;

35

s is zero;

t and u

are each independently zero or 1;

v and w

are each independently zero or 1;

5 one of the R3 and R4 radicals

is hydrogen, F, Cl, Br, I, -CN, -NO₂, -COR₁₄, -SO₂CH₃, alkyl having 1, 2, 3, 4, 5 or 6 carbon atoms, alkoxy having 1, 2, 3 or 4 carbon atoms or -O_x-(CH₂)_y-CF₃,

10 R₁₄ is OH, alkyl having 1, 2, 3, 4, 5 or 6 carbon atoms, alkoxy having 1, 2, 3, 4, 5 or 6 carbon atoms or -O_{aa}-(CH₂)_{bb}-CF₃;

x is zero or 1;

y is zero, 1, 2 or 3;

aa is zero or 1;

15 bb is zero, 1, 2 or 3;

and the other of the R3 and R4 radicals

is -O-phenyl

in which the phenyl radical is unsubstituted or substituted by 1, 2, 3, 4 or 5 radicals selected from the group consisting of F, Cl, Br, NO₂, alkyl having 1, 2, 3 or 4 carbon atoms, -SO_{qq}CH₃, -SO_{rr}CF₃, -CF₃, -OCF₃, -SF₅ or -COR₁₃;

20 qq is zero, 1 or 2,

rr is zero, 1 or 2;

R₅ is hydrogen or F;

25 and salts thereof;

4. A compound of the formula as claimed in one or more of claims 1 to 3, in which:

R₁ is Cl, Br, I, -SO₂R₆ or NO₂;

30 R₆ is OH, F, Cl, Br, I or alkyl having 1, 2, 3 or 4 carbon atoms;

R₂ is hydrogen, F, Cl, Br, I, -CN, -NR₉R₁₀, -OR₁₁, -SR₁₂, -COR₁₃, -(SO_r)_s-(CH₂)_t-(CF₂)_u-CF₃, alkyl having 1, 2, 3, 4, 5 or 6 carbon atoms or cycloalkyl having 3, 4, 5, 6, 7 or 8 carbon atoms, in which 1, 2, 3 or 4 hydrogen atoms may be replaced by fluorine atoms;

35

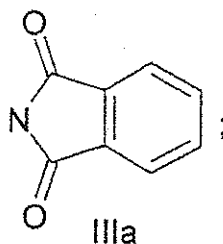
R₉, R₁₀, R₁₁ and R₁₂

are each independently hydrogen, alkyl having 1, 2, 3

or 4 carbon atoms, $-(CH_2)_v-(CF_2)_w-CF_3$, alkylcarbonyl having 1, 2, 3 or 4 carbon atoms or alkylsulfonyl having 1, 2, 3 or 4 carbon atoms;

or

- 5 R9 and R10, together with the nitrogen atom bearing them, form a heterocycle of the formula IIIa:



- 10 R13 is OH, alkyl having 1, 2, 3, 4, 5 or 6 carbon atoms or alkoxy having 1, 2, 3, 4, 5 or 6 carbon atoms;

s is zero;

t and u

are each independently zero or 1;

v and w

are each independently zero or 1;

- 15 one of the R3 and R4 radicals

is hydrogen, F, Cl, Br, I, -CN, -NO₂, -COR₁₄, -SO₂CH₃, alkyl having 1, 2, 3, 4, 5 or 6 carbon atoms, alkoxy having 1, 2, 3 or 4 carbon atoms or -O_x-(CH₂)_y-CF₃,

- 20 R14 is OH, alkyl having 1, 2, 3, 4, 5 or 6 carbon atoms, alkoxy having 1, 2, 3, 4, 5 or 6 carbon atoms or -O_{aa}-(CH₂)_{bb}-CF₃;

x is zero or 1;

y is zero, 1, 2 or 3;

aa is zero or 1;

- 25 bb is zero, 1, 2 or 3;

and the other of the R3 and R4 radicals

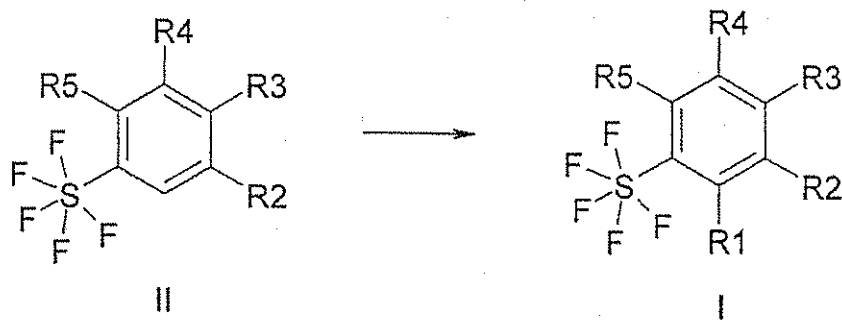
is -O-phenyl

- 30 in which the phenyl radical is unsubstituted or substituted by 1, 2, 3 or 4 radicals selected from the group consisting of F, Cl, Br, NO₂, alkyl having 1, 2, 3 or 4 carbon atoms, -SO₂CH₃, -SO₂CF₃, -CF₃, -OCF₃, -SF₅ or -COR₁₃;

R5 is hydrogen or F;

and salts thereof.

5. A process for preparing compounds of the formula I or salts thereof, which comprises converting compounds of the formula II by electrophilic aromatic substitution to compounds of the formula I



where R1 to R5 are each as defined in claims 1, 2, 3 and/or 4.

6. A compound of the formula I and/or salts thereof as claimed in one or more of claims 1 to 4 for use as a synthetic intermediate.

7. A compound of the formula I and/or salts thereof as claimed in one or more of claims 1 to 4 for use as a synthetic intermediate for the preparation of medicaments, diagnostic aids, liquid crystals, polymers, pesticides, herbicides, fungicides, nematocides, parasiticides, insecticides, acaricides and arthropodocides.