

METHOD FOR PRODUCING AN ELECTRONIC COMPONENT WHICH INCLUDES A SELF-ASSEMBLED MONOLAYER

5 The invention relates to a process for the production of an electronic component comprising a self-assembled monolayer (SAM) using mesogenic compounds containing a spacer group and an anchor group, where the anchor group is an ester derivative of secondary or tertiary alcohols; the present invention furthermore relates to the use of the components in
10 electronic switching elements and to compounds for the production of the SAM.

15 Self-assembled monolayers are known to the person skilled in the art (F. Schreiber: "Structure and growth of self-assembling monolayers", Progress in Surface Science, Oxford, GB, Vol. 65, No. 5-8, 1 November 2000, pages 151-256) and serve, for example, for the modification of electrode surfaces in organic electronics.

20 In computer technology, storage media are required which allow rapid writing and reading access to information stored therein. Solid-state memories or semiconductor memories allow particularly fast and reliable storage media to be achieved, since absolutely no moving parts are necessary. At
25 present, use is mainly made of dynamic random access memory (DRAM). DRAM allows rapid access to the stored information, but this information has to be refreshed regularly, meaning that the stored information is lost when the power supply is switched off.

30 The prior art also discloses non-volatile semiconductor memories, such as flash memory or magnetoresistive random access memory (MRAM), in which the information is retained even after the power supply has been switched off. A disadvantage of flash memory is that writing access takes
35 place comparatively slowly and the memory cells of the flash memory cannot be erased ad infinitum. The lifetime of flash memory is typically limited

to a maximum of one million read/write cycles. MRAM can be used in a similar way to DRAM and has a long lifetime, but this type of memory has not been able to establish itself owing to the difficult production process.

5 A further alternative is memory which works on the basis of memristors. The term memristor is a contraction of the words "memory" and "resistor" and denotes a component which is able to change its electrical resistance reproducibly between high and low electrical resistance. The respective
10 state (high resistance or low resistance) is retained even without a supply voltage, meaning that non-volatile memories can be achieved with memristors.

15 An important alternative application of electrically switchable components arises for the area of neuromorphic or synaptic computing. In computer architectures pursued therein, the information is no longer intended to be processed sequentially in a classical manner. Instead, the aim is to build
20 up the circuits in a highly three-dimensionally interlinked manner in order to be able to achieve information processing analogous to the brain. In artificial neuronal networks of this type, the biological connections between nerve cells (synapses) are then represented by the memristive switching elements. Under certain circumstances, additional intermediate states
25 (between the digital states "1" and "0") may also be of particular benefit here.

WO 2012/127542 A1 and US 2014/008601 A1, for example, disclose
30 organic molecular memories which have two electrodes and an active region which is arranged between the two electrodes. The active region has a molecular layer of electrically conductive aromatic alkynes, whose conductivity can be modified under the influence of an electric field. Similar
35 components based on redox-active bipyridinium compounds are proposed in US 2005/0099209 A1.

The known memories based on a change in conductivity or resistance have the disadvantage that the free-radical intermediates formed by the flow of current through the molecules of the monolayer are in principle susceptible to degradation processes, which has an adverse effect on the lifetime of the components.

Angew. Chem. Int. Ed. 51 (2012), 4658 (H.J. Yoon et al.) and J. Am. Chem. Soc. 136 (2014) 16 - 19 (H.J. Yoon et al.) describe arrangements in which the electronic potential is measured via monolayers of alkyl compounds containing polar end groups. Suitability of such layers for use in switching elements of memristive electronic components cannot be derived therefrom; mesogenic compounds are neither mentioned therein nor is their suitability suggested.

DE102015000120A1 discloses electronic components which are suitable for use in memristive devices. The components contain a self-assembled monolayer of molecules which are able to reorient in an electric field.

An important class of substances which can be aligned in an electric field are mesogenic compounds. Mesogenic compounds are known from the prior art and are compounds which contain one or more mesogenic groups. A mesogenic group is the part of a molecule which, due to the anisotropy of its attractive and repulsive interactions, makes a significant contribution to low-molecular-weight substances forming a liquid-crystalline (LC) mesophase (C. Tschierske, G. Pelzl, S. Diele, Angew. Chem. 2004, 116, 6340 – 6368). The property that mesogenic compounds which carry polar substituents can be aligned and reoriented in an electric field is utilised in practice in liquid-crystal displays (Klasen-Memmer, M., and Hirschmann, H., 2014. Nematic Liquid Crystals for Display Applications. Handbook of Liquid Crystals. 3:II:4:1–25.)

Mesogenic compounds containing a terminal polar anchor group are likewise known in principle from the prior art. JP 2007 177051 A describes mesogenic compounds having positive dielectric anisotropy which are proposed for the derivatisation of iron oxide nanoparticles; the bonding to the particles takes place here through phosphate, phosphonate or carboxylate groups located at the end of the side chain. WO 2013/004372 A1 and WO 2014/169988 A1 disclose mesogenic compounds which carry terminal hydroxyl groups and serve for the derivatisation of substrates for liquid-crystal displays with the aim of homeotropic alignment of the liquid crystal. A corresponding use of dielectrically neutral and positive mesogenic compounds containing polar anchor groups is disclosed in JP2005/002164 A.

The processes described in the above-mentioned DE102015000120A1 for the production of SAMs are dip coating or the process known as the T-BAG method, in which the solvent containing the compound to be applied is slowly evaporated (see E. L. Hanson et al., J. Am. Chem. Soc. 2003, 125, 16074-16080). These lengthy processes are not very suitable for commercial use. Industrially usable processes are, in particular, spin coating, furthermore spray coating, slot-die coating, and conventional printing processes, such as, for example, ink-jet printing, screen printing, micro-contact stamp printing, and in addition deposition from the gas phase. In particular on use of monolayer-forming compounds which contain free acid groups as anchor groups, the problem arises that they are only sufficiently soluble in highly polar solvents, such as, for example, THF, ethanol or isopropanol. These solvents compete with the monolayer-forming compounds for bonding to the substrates and thus reduce the quality of the monolayers.

The choice of industrially usable solvents for the above-mentioned processes is limited. Examples of such solvents are non-polar solvents, such as hydrocarbons (decalin, xylene), halogenated hydrocarbons (chlorobenzene, trichloroethylene, Solkan-365 (HFC-365mfc, 1,1,1,3,3-penta-

5 fluorobutane), or weakly polar esters, ethers and ketones (propylene glycol monomethyl ether acetate (PGMEA), propylene glycol monomethyl ether (PGME), methyl amyl ketone (MAK), ethyl acetate, methyl tert-butyl ether (MTBE), cyclohexanone). The disadvantage of these solvents is the poor solubility of compounds from the prior art for the production of SAMs, particularly in the case of compounds containing strongly polar, acidic anchor groups, such as, for example, phosphonic acid groups.

10 For deposition from the gas phase, it is necessary that the compounds can be evaporated without decomposition for the formation of a monolayer, which often represents a problem, in particular in the case of free acids, such as sulfonic acids and phosphonic acids, since strongly acidic groups
15 can cause autocatalytic decomposition on heating of a substance.

An object to be achieved consists in indicating an improved process for the production of a component.

20 A further object is to search for novel compounds which are suitable for the production of components using methods that are conventional in the memory industry, in particular spin coating or deposition from the gas phase.

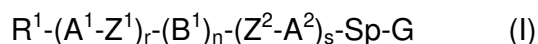
25 It has now been found that these objects can be achieved, at least in part, if the components are produced by a process in accordance with independent Claim 1.

30 The invention relates to a process for the production of a component, comprising at least the following steps:

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- (1) provision of a substrate having a substrate surface,
 - (2) application of a solution comprising one or more compounds of the formula I to the substrate surface,

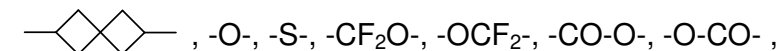
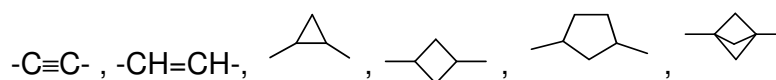
(3) heating of the substrate to a temperature in the range from 60°C to 300°C,

where formula I is defined as follows:



in which

R^1 denotes H, an alkyl or alkoxy radical having 1 to 15 C atoms, where, in addition, one or more CH_2 groups in these radicals may each be replaced, independently of one another, by



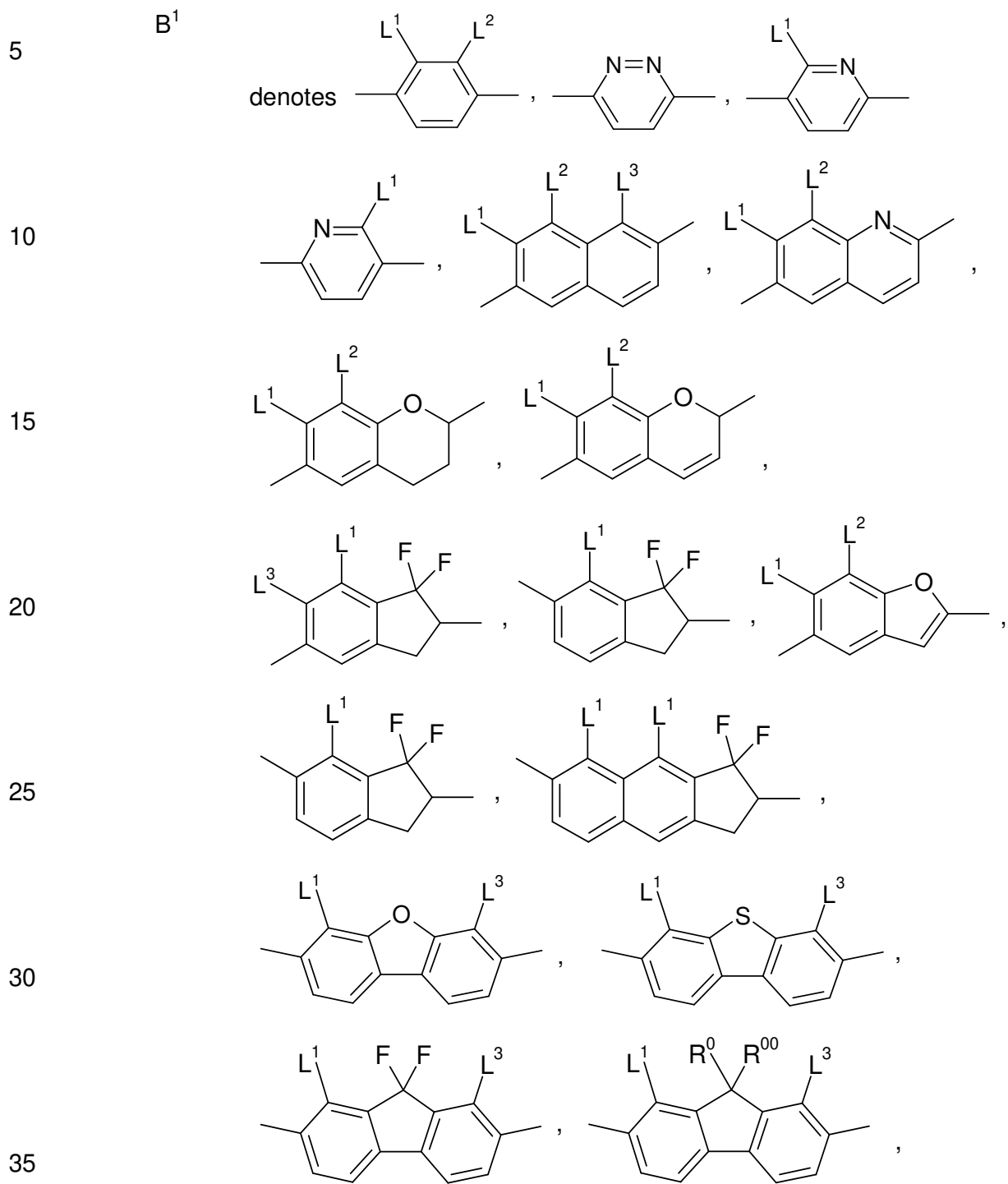
$-SiR^0R^{00}-$, $-NH-$, $-NR^0-$ or $-SO_2-$ in such a way that O atoms are not linked directly to one another, and in which, in addition, one or more H atoms may be replaced by halogen, CN, SCN or SF_5 ,

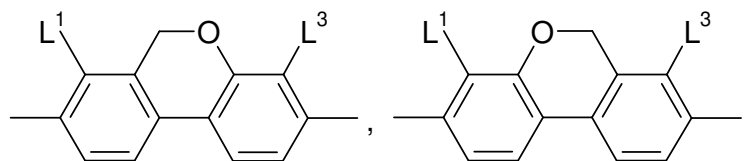
R^0 , R^{00} denote, identically or differently, an alkyl or alkoxy radical having 1 to 15 C atoms, in which, in addition, one or more H atoms may be replaced by halogen,

A^1 , A^2 on each occurrence, identically or differently, denote an aromatic, heteroaromatic, alicyclic or heteroaliphatic ring having 4 to 25 ring atoms, which may also contain condensed rings and which may be mono- or polysubstituted by Y,

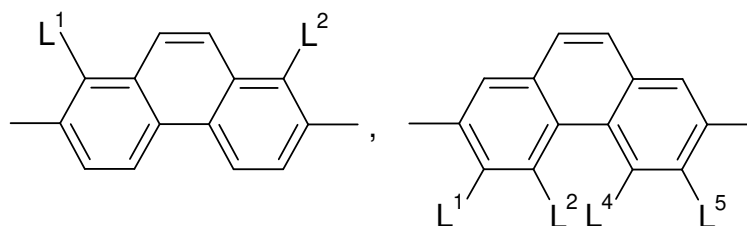
Y on each occurrence, identically or differently, denotes F, Cl, CN, SCN, SF_5 or straight-chain or branched, in each case optionally fluorinated, alkyl, alkoxy, alkylcarbonyl,

alkoxycarbonyl, alkylcarbonyloxy or alkoxycarbonyloxy having
1 to 12 C atoms,





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where the groups may be oriented in both directions,

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L^1 to L^5 , independently of one another, denote F, Cl, Br, I, CN, SF_5 , CF_3 or OCF_3 , preferably Cl or F, where L^3 may alternatively also denote H,

20

Z^1 , Z^2 on each occurrence, identically or differently, denote a single bond, $-CF_2O-$, $-OCF_2-$, $-CF_2S-$, $-SCF_2-$, $-CH_2O-$, $-OCH_2-$, $-C(O)O-$, $-OC(O)-$, $-C(O)S-$, $-SC(O)-$, $-CH_2-$, $-(CH_2)_2-$, $-(CH_2)_3-$, $-(CH_2)_4-$, $-CF_2-$, $-CF_2CF_2-$, $-CF_2CH_2-$, $-CH_2CF_2-$, $-CH=CH-$, $-CF=CF-$, $-CF=CH-$, $-CH=CF-$, $-(CH_2)_3O-$, $-O(CH_2)_3-$, $-C\equiv C-$, $-O-$, $-S-$, $-C=N-$, $-N=C-$, $-N=N-$, $-N=N(O)-$, $-N(O)=N-$ or $-N=C-C=N-$,

25

Sp denotes a spacer group or a single bond,

30

G denotes $-SO_2OR^V$, $-OP(O)(OR^V)_2$, $-PO(OR^V)_2$, $-C(OH)(PO(OR^V)_2)_2$, $-COOR^V$ or $-Si(OR^V)_3$,

35

R^V denotes secondary or tertiary alkyl having 3 to 20 C atoms,

r and s, independently of one another, denote 0, 1, 2 or 3,

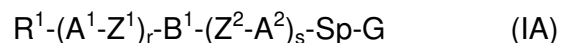
where $r + s \leq 4$, and

5 n denotes 0 or 1.

The invention furthermore relates to a component for use in an electronic element containing a self-assembled monolayer, formed and set up for the adoption of two switching states, where the component has been produced
10 by the above-mentioned process according to the invention, with the proviso that the self-assembled monolayer has been produced from one or more compounds of the above-mentioned formula I, for which n is equal to 1 and the other groups and parameters have the meanings indicated in
15 Claim 1.

The invention furthermore relates to the use of the component according to the invention in a memristive electronic switching element.

20 The invention furthermore relates to compounds of the formula IA



25 in which the groups and parameters occurring have the meanings indicated above.

The compounds of the formulae I and IA are highly soluble in the above-mentioned solvents, which are used in industrially usable processes, such
30 as, for example, spin coating. The process according to the invention can thus be employed under conditions as have become established in the industrial production of memory chips. The components produced in this way have excellent applicational properties, in particular they are suitable
35 for the production of switching elements for memristive devices, and are compatible with the standard methods and processes, switching param-

eters and design rules of silicon electronics (CMOS). The switching elements produced in this way have a high degree of reversibility of the switching operation without "fatigue phenomena".

5 Surprisingly, it has been found that the components produced by the present process have the same advantageous applicational properties as through use of the corresponding free protic (acidic) compounds (in which, for example, G denotes $-P(O)(OH)_2$).

10 The compounds of the formula IA are preferably mesogenic and have negative dielectric anisotropy.

Brief description of the drawings

15 Fig. 1 shows the current/voltage curve of a component produced by the process according to the invention,
Fig. 2 shows the current/voltage curve of a component produced by dip coating with a comparative compound containing a phosphonic acid anchor group.

20 The term "mesogenic group" is known to the person skilled in the art and is defined in accordance with C. Tschierske, G. Pelzl, S. Diele, Angew. Chem. 2004, 116, 6340-6368, as the part of a molecule or macromolecule
25 which, due to the anisotropy of its attracting and repelling interactions, makes a significant contribution to the low-molecular-weight or polymeric substances forming a liquid-crystalline mesophase. The majority of mesogenic groups consist of rigid rod- or disc-shaped units.

30 A mesogenic compound ("mesogen" for short) is characterised in that it contains one or more mesogenic groups. The mesogenic compounds here do not necessarily have to have a liquid-crystalline phase themselves.

35 The dielectric anisotropy $\Delta\epsilon$ of a uniaxial mesogenic compound is defined as the difference between the dielectric constants parallel ($\epsilon_{||}$) and perpen-

dicular ($\epsilon_{\perp}$) to the longitudinal axis of the molecule. In the case of dielectrically negative compounds, it follows that $\Delta\epsilon = (\epsilon_{\parallel} - \epsilon_{\perp}) < 0$.

5 An anchor group in the sense of the present invention is a functional group by means of which the mesogenic compound is adsorbed onto or bonded to the surface of the substrate by physisorption, chemisorption or by chemical reaction.

10 A spacer group in the sense of the present invention is a flexible chain between mesogenic group and anchor group which causes a separation between these sub-structures and, owing to its flexibility, at the same time improves the mobility of the mesogenic group after bonding to a substrate.

15 The material in the sense of the present invention comprises one or more compounds of the formula I as defined above in a total concentration of 90 to 100%. The material preferably comprises one or more compounds of the formula IA in a total concentration of 50% to 100%. The material may com-
20 prise up to 5% of further surface-active compounds which are suitable for the formation of a self-assembled monolayer, preferably selected from the corresponding free phosphonic acids and sulfonic acids of the formula I.

25 If R^1 represents an alkyl radical, this is straight-chain or branched and has 1 to 15 C atoms. R^1 is preferably straight-chain and has, unless indicated otherwise, 1, 2, 3, 4, 5, 6 or 7 C atoms and is accordingly preferably methyl, ethyl, propyl, butyl, pentyl, hexyl or heptyl.

30 If R^1 represents an alkoxy radical, this is straight-chain or branched and contains 1 to 15 C atoms. R^1 is preferably straight-chain and has, unless indicated otherwise, 1, 2, 3, 4, 5, 6 or 7 C atoms and is accordingly preferably methoxy, ethoxy, propoxy, butoxy, pentoxy, hexoxy or heptoxy.
35

R¹ in formula I can furthermore be an alkenyl radical having 2 to 15 C atoms, which is straight-chain or branched and contains at least one C-C double bond. It is preferably straight-chain and has 2 to 7 C atoms. Accordingly, it is preferably vinyl, prop-1- or -2-enyl, but-1-, -2- or -3-enyl, pent-1-,
5 -2-, -3- or -4-enyl, hex-1-, -2-, -3-, -4- or -5-enyl, hept-1-, -2-, -3-, -4-, -5- or -6-enyl. If the two C atoms of the C-C double bond are substituted, the alkenyl radical can be in the form of E and/or Z isomer (trans/cis). In general, the respective E isomers are preferred. Of the alkenyl radicals, prop-2-
10 enyl, but-2- and -3-enyl, and pent-3- and -4-enyl are particularly preferred. Of the alkenyl radicals for use in accordance with a further aspect of the present invention with the aim of activation of the molecular layer, terminal alkenyls are preferred

15 R¹ in formula I can also be an alkynyl radical having 2 to 15 C atoms, which is straight-chain or branched and contains at least one C-C triple bond. 1- and 2-propynyl and 1-, 2- and 3-butynyl are preferred.

20 Preferred aryl groups are derived, for example, from the parent structures benzene, naphthalene, tetrahydronaphthalene, 9,10-dihydrophenanthrene, fluorene, indene and indane.

25 Preferred heteroaryl groups are, for example, five-membered rings, such as, for example, furan, thiophene, selenophene, oxazole, isoxazole, 1,2-thiazole, 1,3-thiazole, 1,2,3-oxadiazole, 1,2,4-oxadiazole, 1,2,5-oxadiazole, 1,3,4-oxadiazole, 1,2,3-thiadiazole, 1,2,4-thiadiazole, 1,2,5-thiadiazole and
30 1,3,4-thiadiazole, six-membered rings, such as, for example, pyridine, pyridazine, pyrimidine, pyrazine, 1,3,5-triazine, 1,2,4-triazine and 1,2,3-triazine, or condensed rings, such as, for example, indole, isoindole, indolizine, indazole, benzimidazole, benzotriazole, purine, naphthimidazole, benzoxazole, naphthoxazole, benzothiazole, benzofuran, isobenzofuran,
35 dibenzofuran, thieno[2,3b]thiophene, thieno[3,2b]thiophene, dithienothiophene, isobenzothiophene, dibenzothiophene, benzothiadiazothiophene,

2H-chromen (2H-1-benzopyran), 4H-chromene (4H-1-benzopyran) and coumarin (2H-chromen-2-one), or combinations of these groups.

5 Preferred cycloaliphatic groups are cyclobutane, cyclopentane, cyclohexane, cyclohexene, cycloheptane, decahydronaphthalene, bicyclo[1.1.1]pentane, bicyclo[2.2.2]octane, spiro[3.3]heptane and octahydro-4,7-methanoindane.

10 Preferred heteroaliphatic groups are tetrahydrofuran, dioxolane, tetrahydrothiofuran, pyran, dioxane, dithiane, silinane, piperidine and pyrrolidine.

15 A¹ and A², independently of one another and identically or differently on each occurrence, are particularly preferably selected from the following groups:

20 a) 1,4-phenylene, in which, in addition, one or two CH groups may be replaced by N and in which, in addition, one or more H atoms may be replaced by Y,

25 b) the group consisting of trans-1,4-cyclohexylene and 1,4-cyclohexenylene, in which, in addition, one or more non-adjacent CH₂ groups may be replaced by -O- and/or -S- and in which, in addition, one or more H atoms may be replaced by Y, and

30 c) the group consisting of 1,3-dioxolane-2,4-diyl, tetrahydrofuran-2,5-diyl, cyclobutane-1,3-diyl, 1,4-bicyclo[2.2.2]octanediyl, piperidine-1,5-diyl and thiophene-2,5-diyl, in which, in addition, one or more H atoms may be replaced by Y,

35 where Y has the meaning indicated above under formula I and preferably denotes F, Cl, CN or CF₃.

In formula I, Sp preferably denotes a spacer group.

Preferred spacer groups Sp are selected from the formula Sp'-X', so that the radical G-Sp- corresponds to the formula G-Sp'-X', where

5

Sp' denotes straight-chain or branched alkylene having 1 to 20, preferably 1 to 12 C atoms, which is optionally mono- or poly-substituted by F, Cl, Br, I or CN and in which, in addition, one or more non-adjacent CH₂ groups may each be replaced, independently of one another, by -O-, -S-, -NH-, -NR⁰-, -SiR⁰⁰R⁰⁰⁰-, -CO-, -COO-, -OCO-, -OCO-O-, -S-CO-, -CO-S-, -NR⁰⁰-CO-O-, -O-CO-NR⁰⁰-, -NR⁰⁰-CO-NR⁰⁰-, -CH=CH- or -C≡C- in such a way that O and/or S atoms are not linked directly to one another,

15

X' denotes -O-, -S-, -CO-, -COO-, -OCO-, -O-COO-, -CO-NR⁰⁰-, -NR⁰⁰-CO-, -NR⁰⁰-CO-NR⁰⁰-, -OCH₂-, -CH₂O-, -SCH₂-, -CH₂S-, -CF₂O-, -OCF₂-, -CF₂S-, -SCF₂-, -CF₂CH₂-, -CH₂CF₂-, -CF₂CF₂-, -CH=N-, -N=CH-, -N=N-, -CH=CR⁰⁰-, -CY^x=CY^{x'}-, -C≡C-, -CH=CH-COO-, -OCO-CH=CH- or a single bond,

20

R⁰⁰

25

and R⁰⁰⁰ each, independently of one another, denote H or alkyl having 1 to 12 C atoms, and

Y^x and Y^{x'} each, independently of one another, denote H, F, Cl or CN.

30

X' is preferably -O-, -S-, -CO-, -COO-, -OCO-, -O-COO-, -CO-NR⁰-, -NR⁰-CO-, -NR⁰-CO-NR⁰- or a single bond.

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Preferred spacer groups Sp' are -(CH₂)_{p1}-, -(CF₂)_{p1}-, -(CH₂CH₂O)_{q1}-CH₂CH₂-, -(CF₂CF₂O)_{q1}-CF₂CF₂-, -CH₂CH₂-S-CH₂CH₂-, -CH₂CH₂-NH-CH₂CH₂- or

$-(\text{SiR}^{00}\text{R}^{000}-\text{O})_{p1-}$, in which $p1$ is an integer from 1 to 12, $q1$ is an integer from 1 to 3, and R^{00} and R^{000} have the meanings indicated above.

5 Particularly preferred groups $-\text{X}'-\text{Sp}'-$ are $-(\text{CH}_2)_{p1-}$, $-\text{O}-(\text{CH}_2)_{p1-}$, $-(\text{CF}_2)_{p1-}$, $-\text{O}(\text{CF}_2)_{p1-}$, $-\text{OCO}-(\text{CH}_2)_{p1-}$ and $-\text{OC}(\text{O})\text{O}-(\text{CH}_2)_{p1-}$, in which $p1$ has the meaning indicated above.

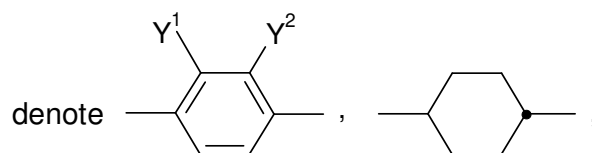
10 Particularly preferred groups Sp' are, for example, in each case straight-chain ethylene, propylene, butylene, pentylene, hexylene, heptylene, octylene, nonylene, decylene, undecylene, dodecylene, octadecylene, perfluoroethylene, perfluoropropylene, perfluorobutylene, perfluoropentylene, perfluorohexylene, perfluoroheptylene, perfluorooctylene, perfluorononylene, perfluorodecylene, perfluoroundecylene, perfluorododecylene, perfluorooctadecylene, ethylenoxyethylene, methylenoxybutylene, ethylene-thioethylene, ethylene-N-methyliminoethylene, 1-methylalkylene, ethenylene, propenylene and butenylene.

20 Particularly preferred sub-formulae of the formula IA are the sub-formulae IAa to IAf shown below:

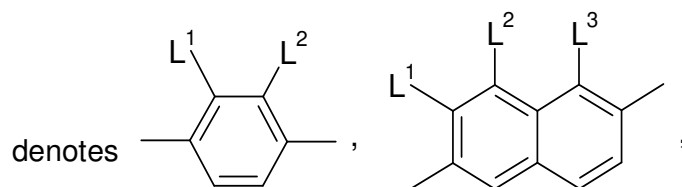
25	$\text{R}^1-\text{B}^1-\text{Sp}-\text{G}$	IAa
	$\text{R}^1-(\text{A}^1-\text{Z}^1)-\text{B}^1-\text{Sp}-\text{G}$	IAb
	$\text{R}^1-(\text{A}^1-\text{Z}^1)_2-\text{B}^1-\text{Sp}-\text{G}$	IAc
30	$\text{R}^1-\text{B}^1-(\text{Z}^2-\text{A}^2)-\text{Sp}-\text{G}$	IAd
	$\text{R}^1-\text{B}^1-(\text{Z}^2-\text{A}^2)_2-\text{Sp}-\text{G}$	IAe
35	$\text{R}^1-(\text{A}^1-\text{Z}^1)-\text{B}^1-(\text{Z}^2-\text{A}^2)-\text{Sp}-\text{G}$	IAf

in which R^1 , A^1 , A^2 , B^1 , Z^1 , Z^2 , Sp and G have the meanings indicated above and preferably

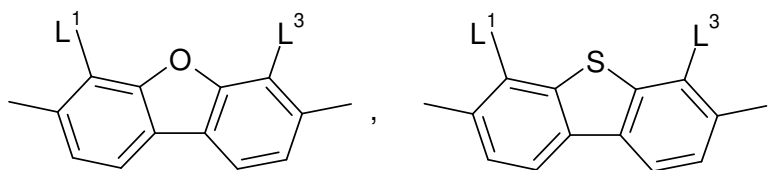
5 A^1 and A^2



10 B^1



15



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where the groups may be oriented in both directions,

R^1 denotes alkyl having 1-15 C atoms, preferably having 1-7 C atoms, in particular CH_3 , C_2H_5 , $n-C_3H_7$, $n-C_4H_9$, $n-C_5H_{11}$, $n-C_6H_{13}$ or $n-C_7H_{15}$.

25

L^1 and L^2 , independently of one another, denote Cl or F,

L^3 denotes F,

30

Y^1 and Y^2 , independently of one another, denote H, Cl or F,

Z^1 , Z^2 , independently of one another, denote a single bond, $-CF_2O-$, $-OCF_2-$, $-CH_2O-$, OCH_2- or $-CH_2CH_2-$,

35

Sp denotes unbranched 1,ω-alkylene having 1 to 12 C atoms,

G denotes -CH=CH₂, -OH, -SH, -SO₂OH, -OP(O)(OH)₂,
-PO(OH)₂, -COH(PO(OH)₂)₂, -COOH, -Si(OR)₃ or -SiCl₃.

5

In a further preferred embodiment, in the compounds of the formulae IAa to IAf,

10

Sp denotes unbranched 1,ω-perfluoroalkylene having 1 to 12 C atoms,

where R¹, A¹, A², B¹, Z¹, Z² and G have the meanings indicated above.

15

Very particularly preferred sub-formulae of the formula IA are the sub-formulae IAa, IAb and IAd.

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In a further embodiment, the material for the production of the monolayer according to the invention additionally comprises one or more compounds of the formula Ig



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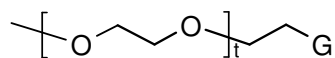
in which R² has the meaning indicated for R¹ above under formula I and G has the meaning indicated above under formula I.

The one or more compounds of the formula Ig are preferably selected from the compounds of the formulae Ig-1 to Ig-3

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Ig-3

in which

G denotes $-\text{PO}(\text{OR}^V)_2$ or $-\text{SO}_2\text{OR}^V$,

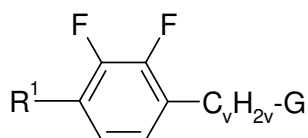
R^V denotes secondary or tertiary alkyl having 3 to 20 C atoms,

r denotes an integer from 1 to 20,

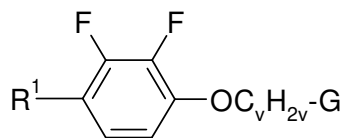
s denotes an integer from 1 to 18, and

t denotes an integer from 1 to 4.

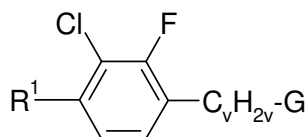
Examples of preferred compounds of the formulae IAa to IAf are shown below:



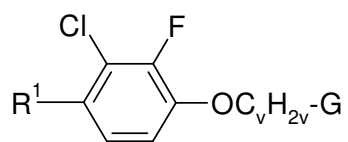
IAa-1



IAa-2

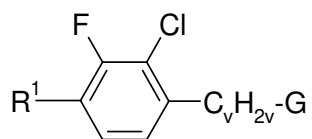


IAa-3



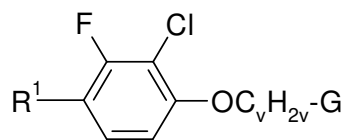
IAa-4

5



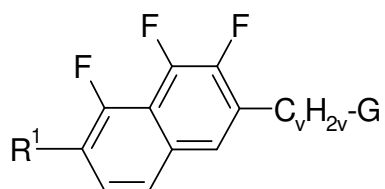
IAa-5

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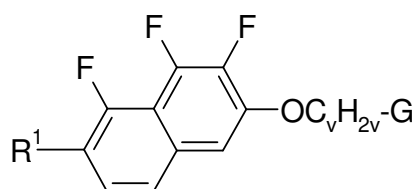
IAa-6

15



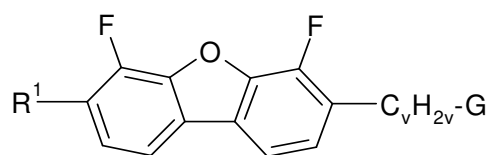
IAa-7

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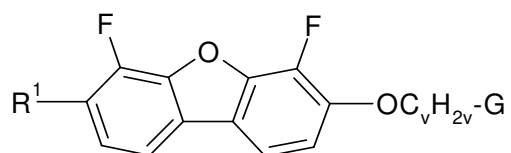
IAa-8

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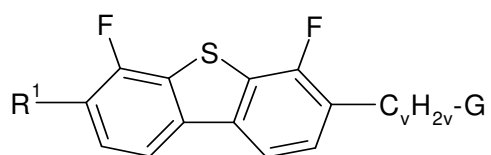
IAa-9

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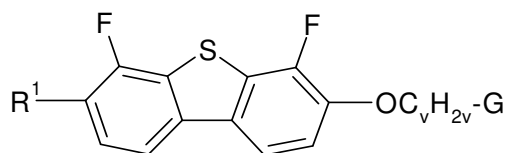
IAa-10

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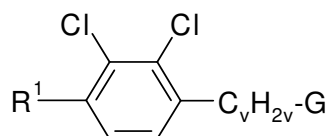
IAa-11

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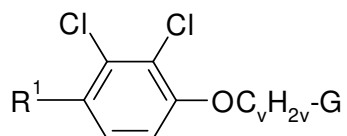
IAa-12

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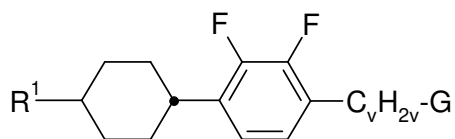
IAa-13

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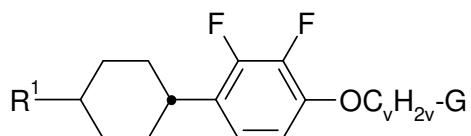
IAa-14

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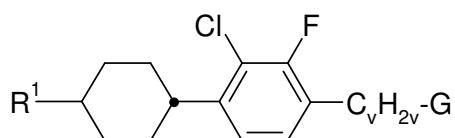
IAb-1

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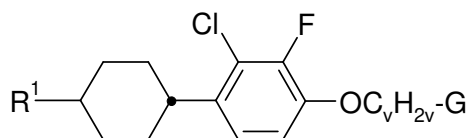
IAb-2

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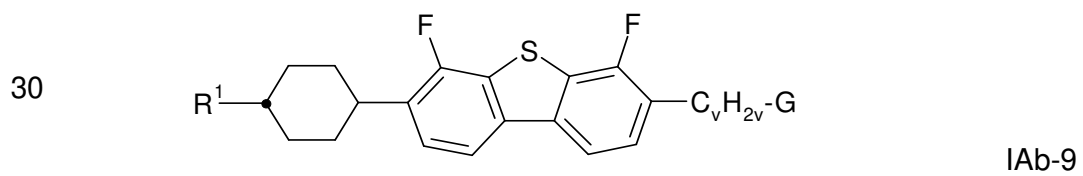
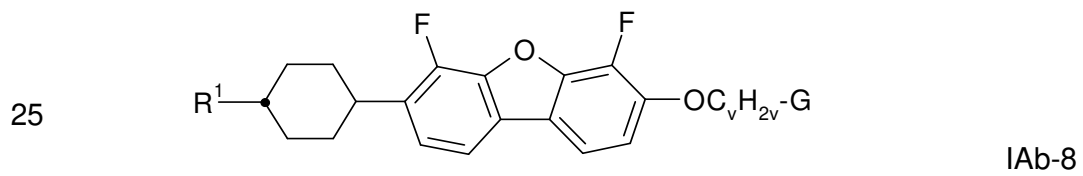
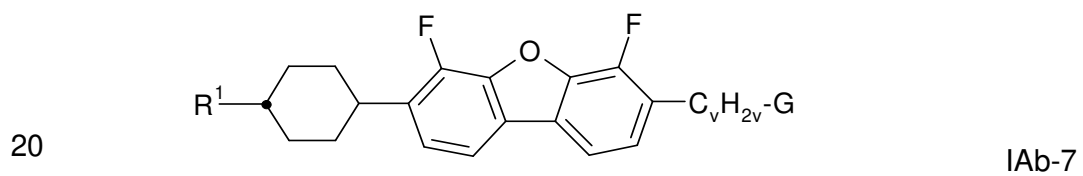
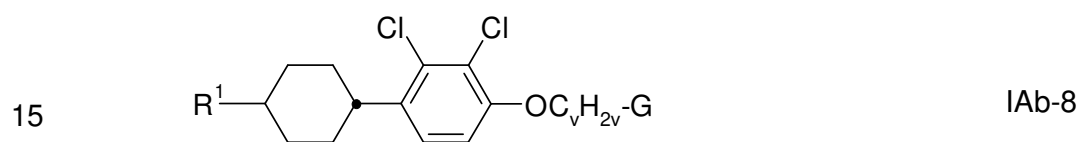
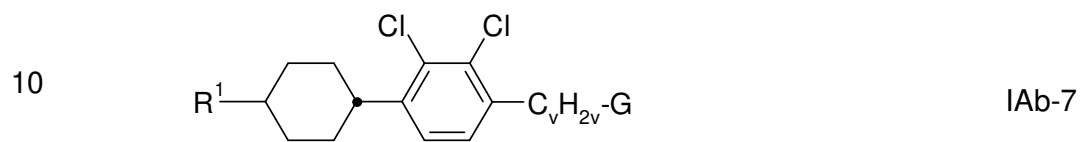
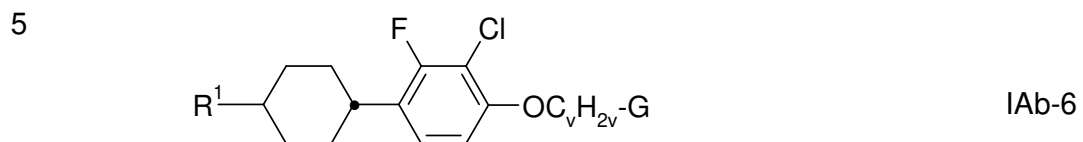
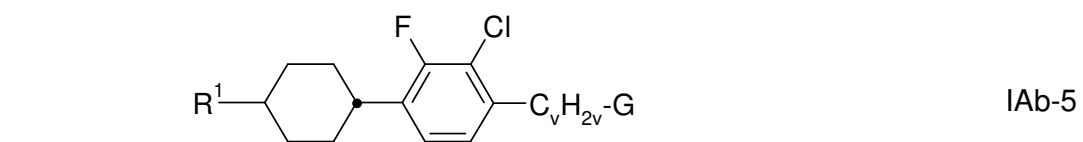


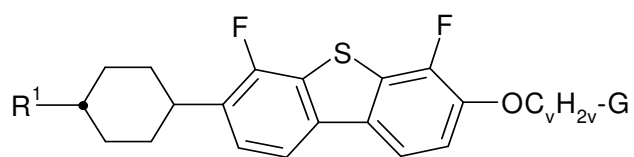
IAb-3

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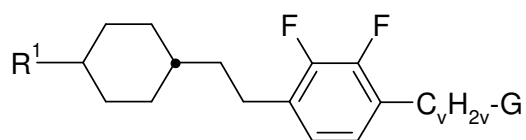
IAb-4





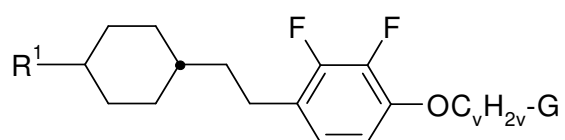
IAb-10

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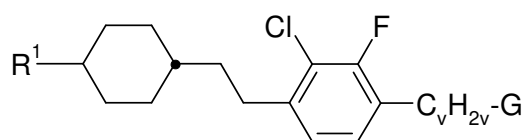
IAb-11

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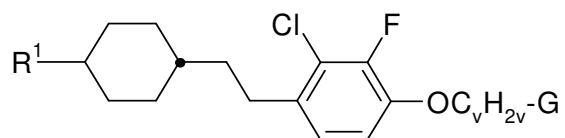
IAb-12

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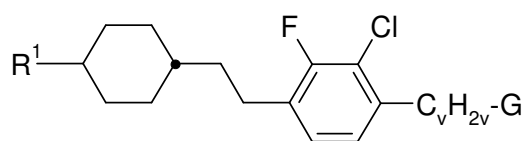
IAb-13

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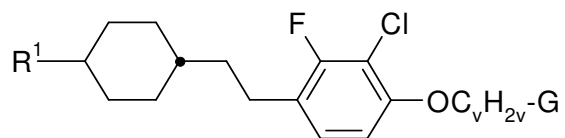
IAb-14

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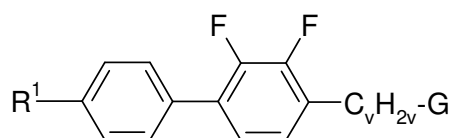
IAb-15

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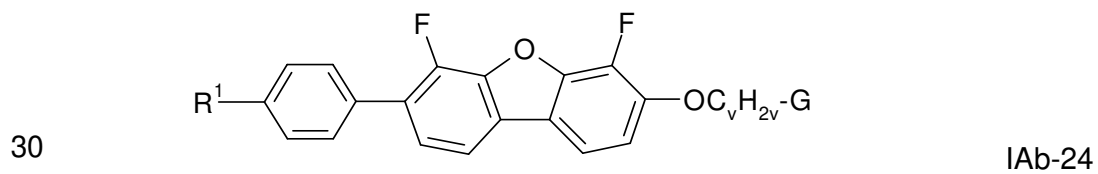
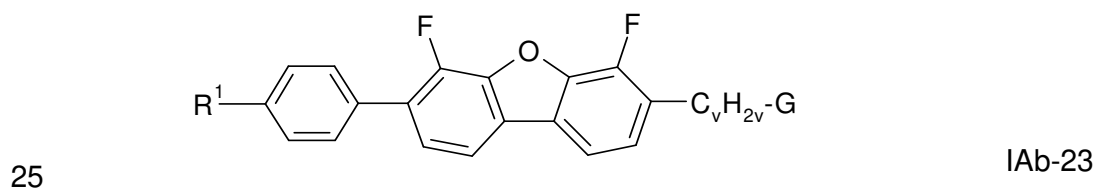
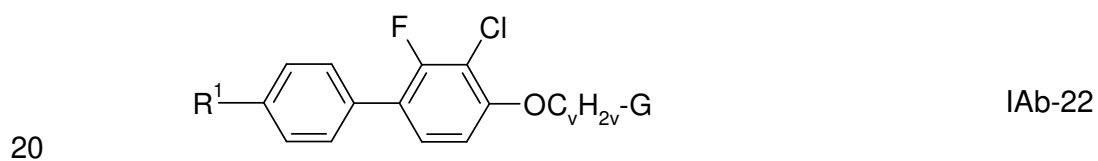
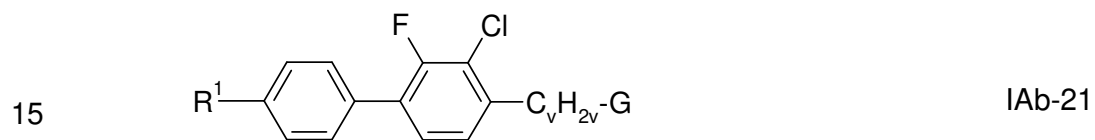
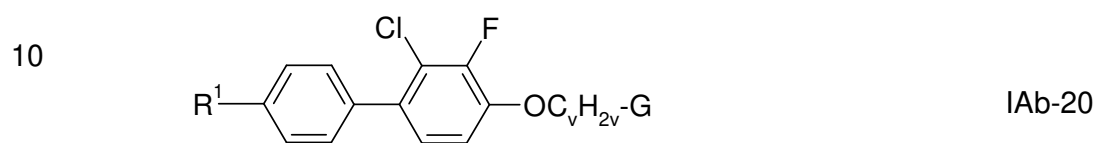
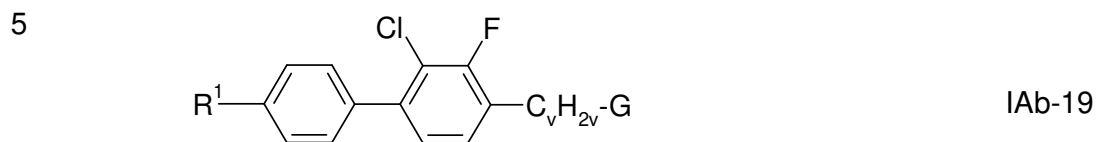
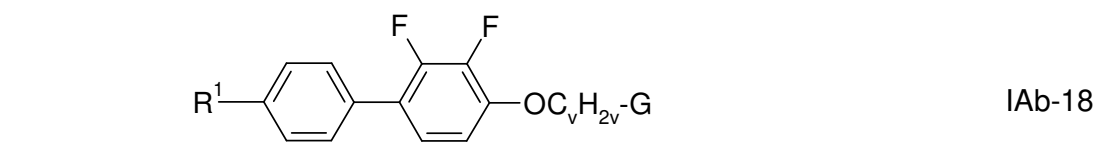


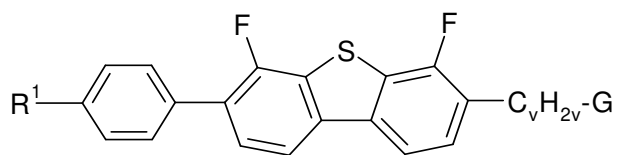
IAb-16

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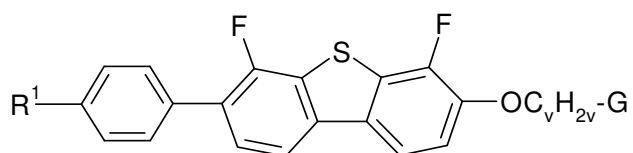
IAb-17





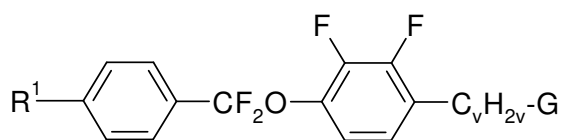
IAb-25

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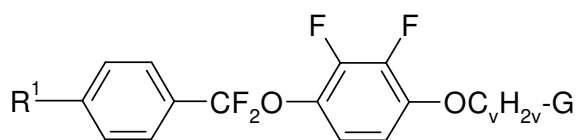
IAb-26

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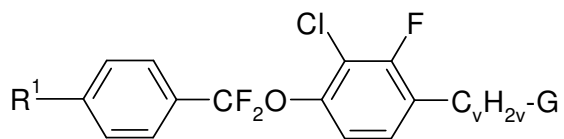
IAb-27

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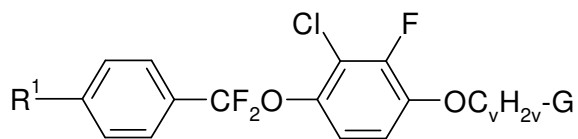
IAb-28

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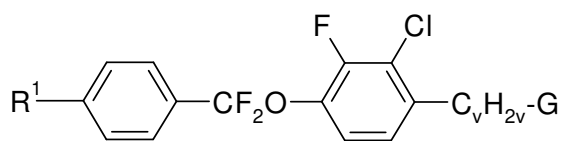
IAb-29

25



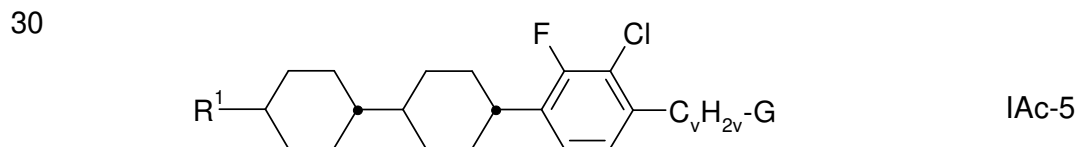
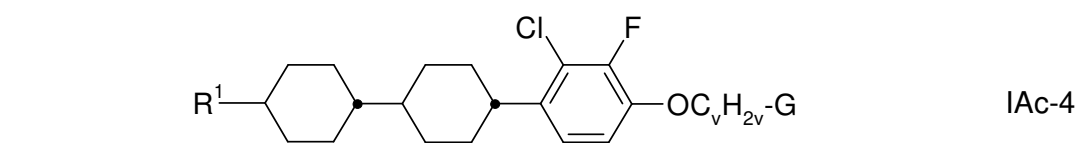
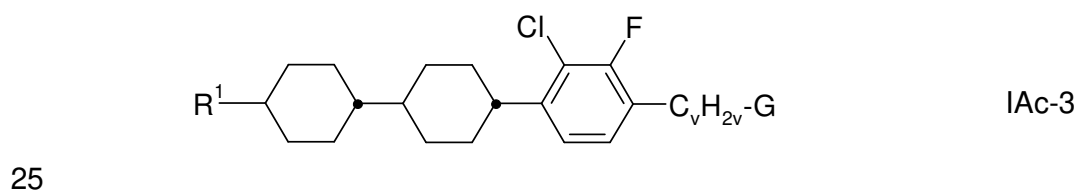
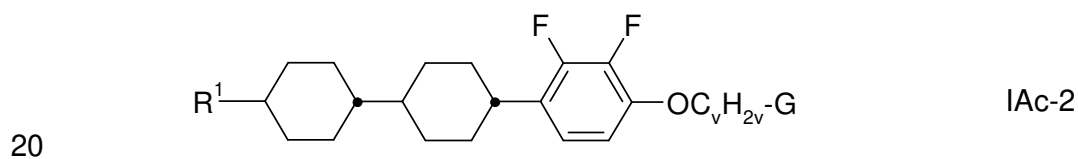
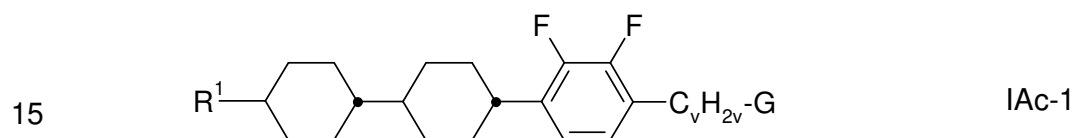
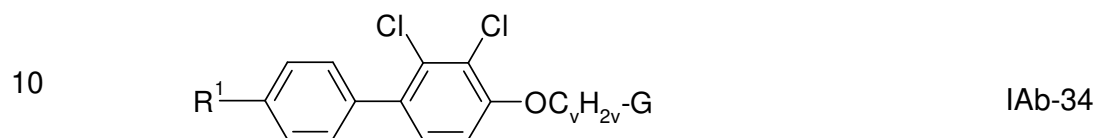
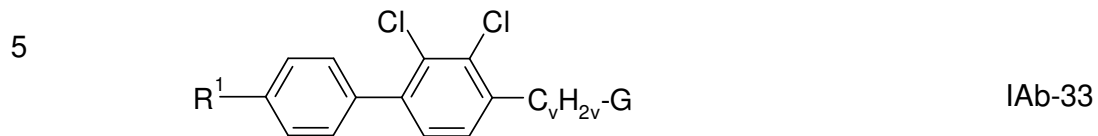
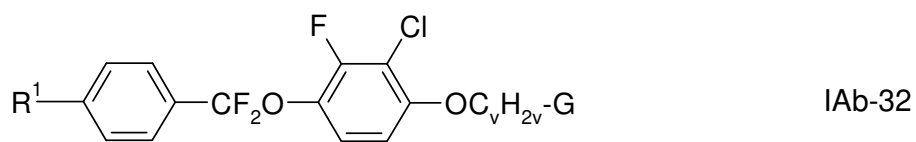
IAb-30

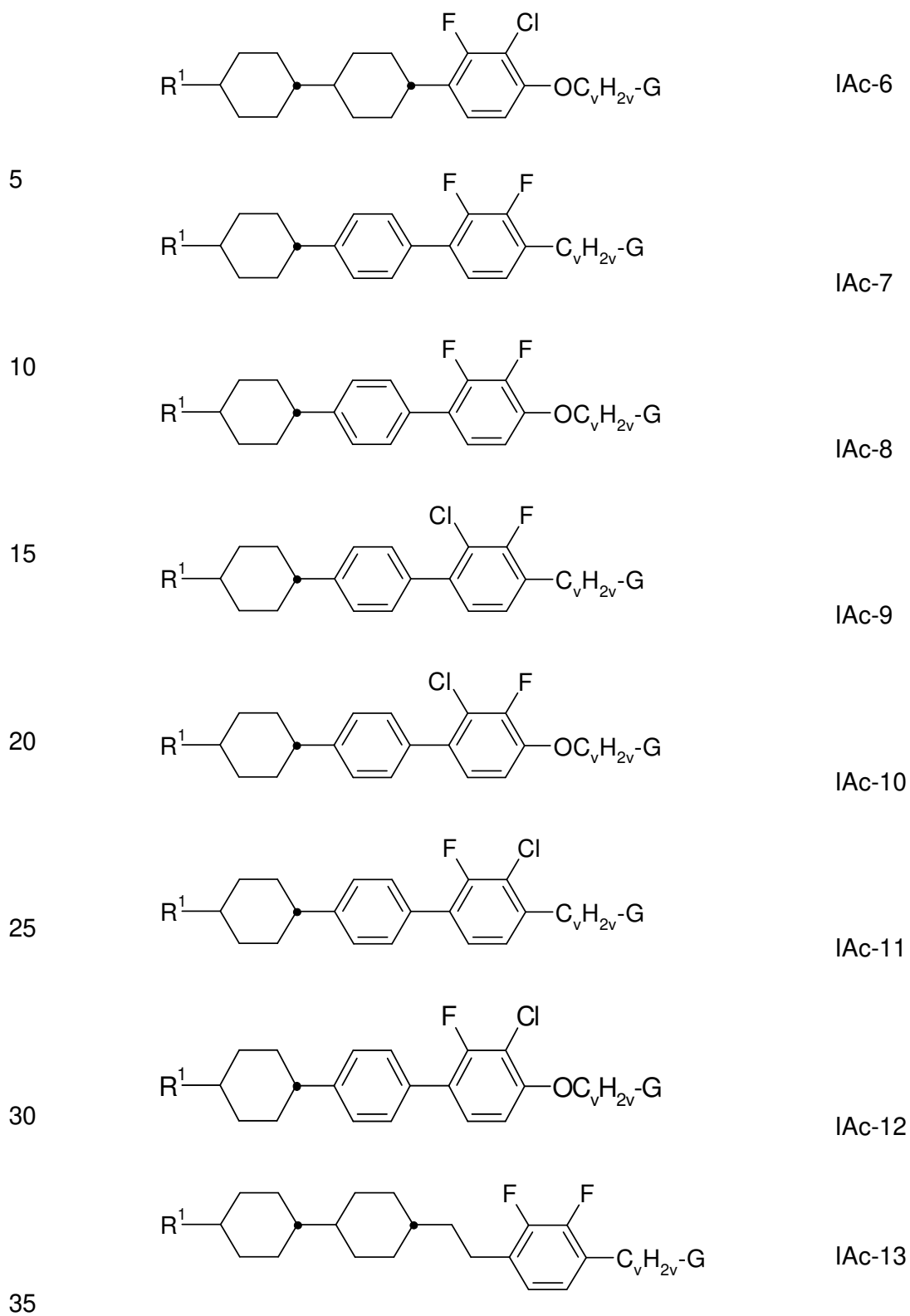
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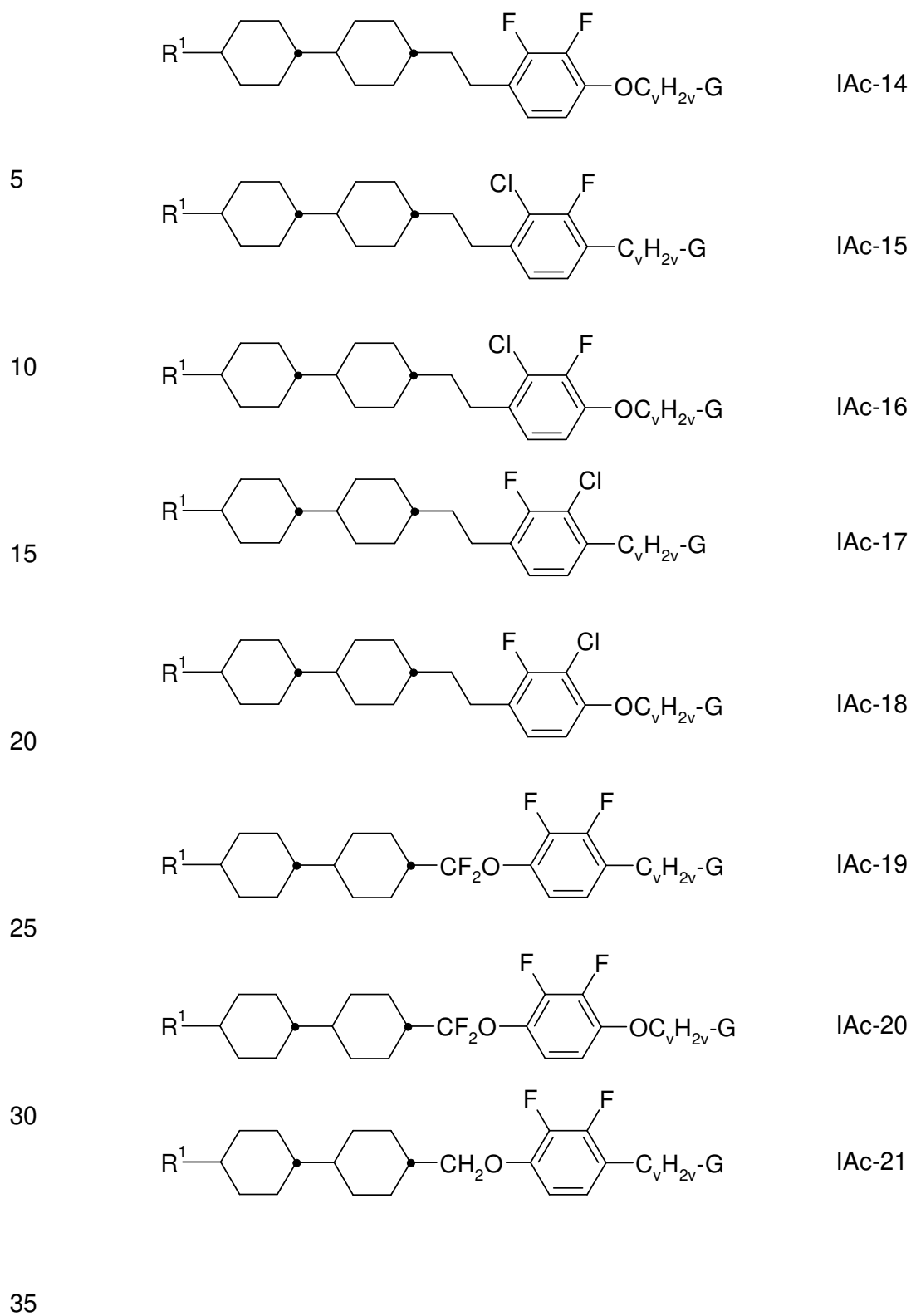


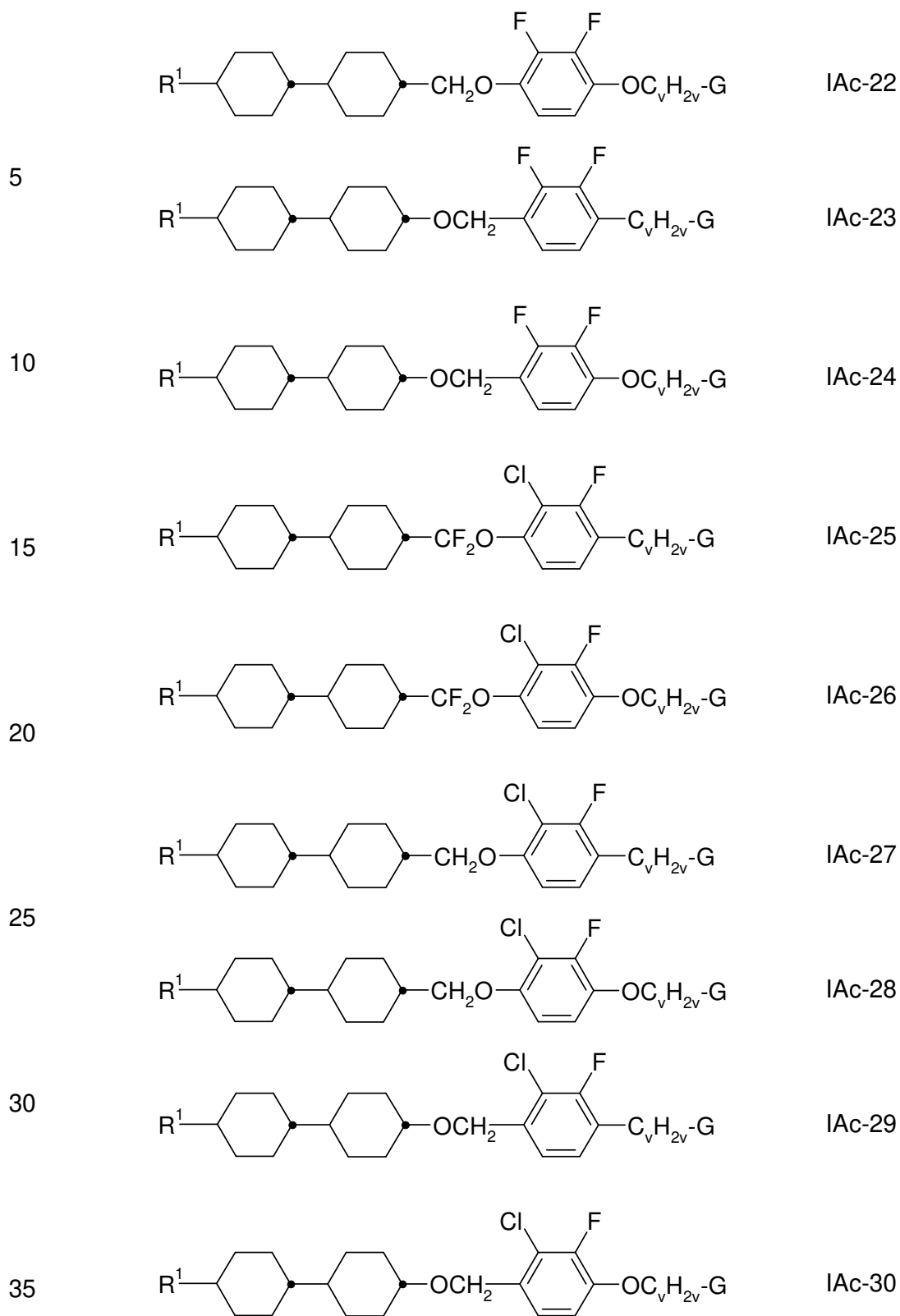
IAb-31

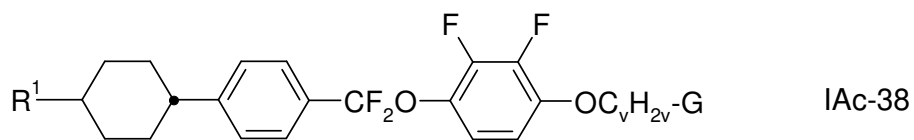
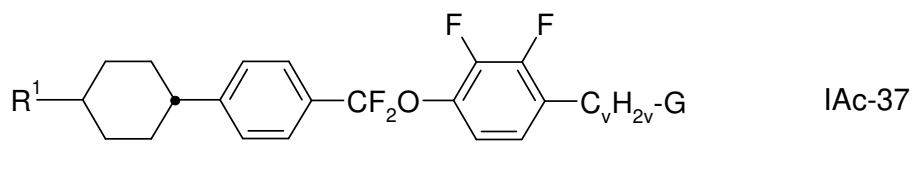
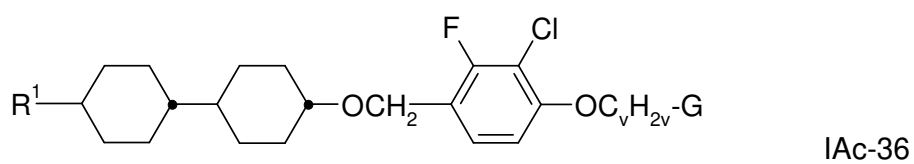
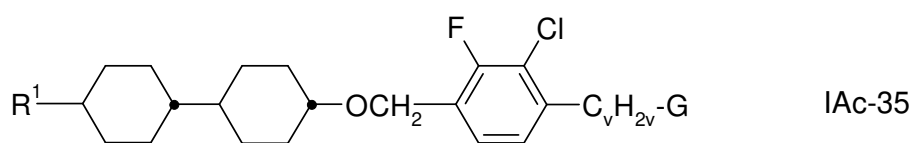
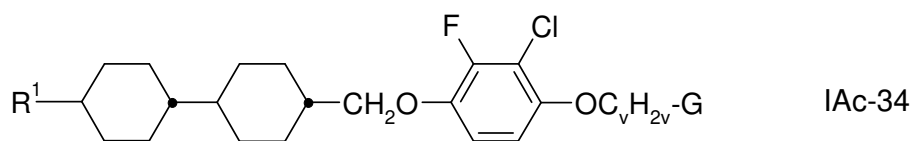
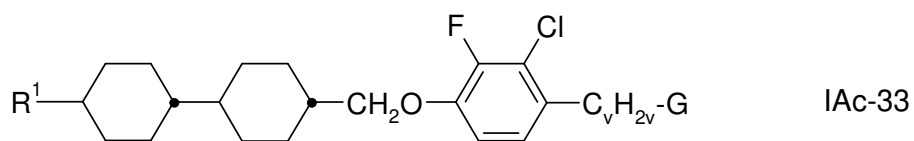
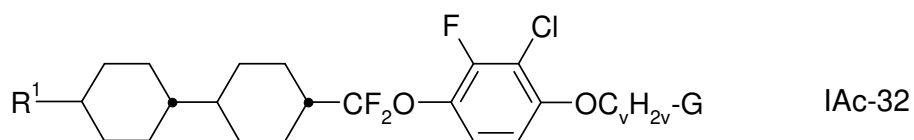
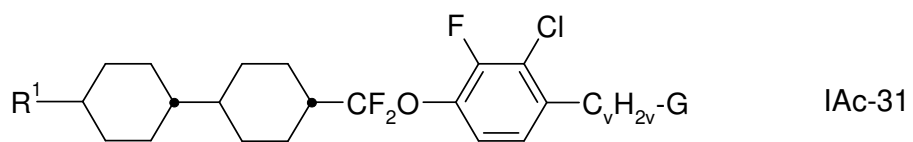
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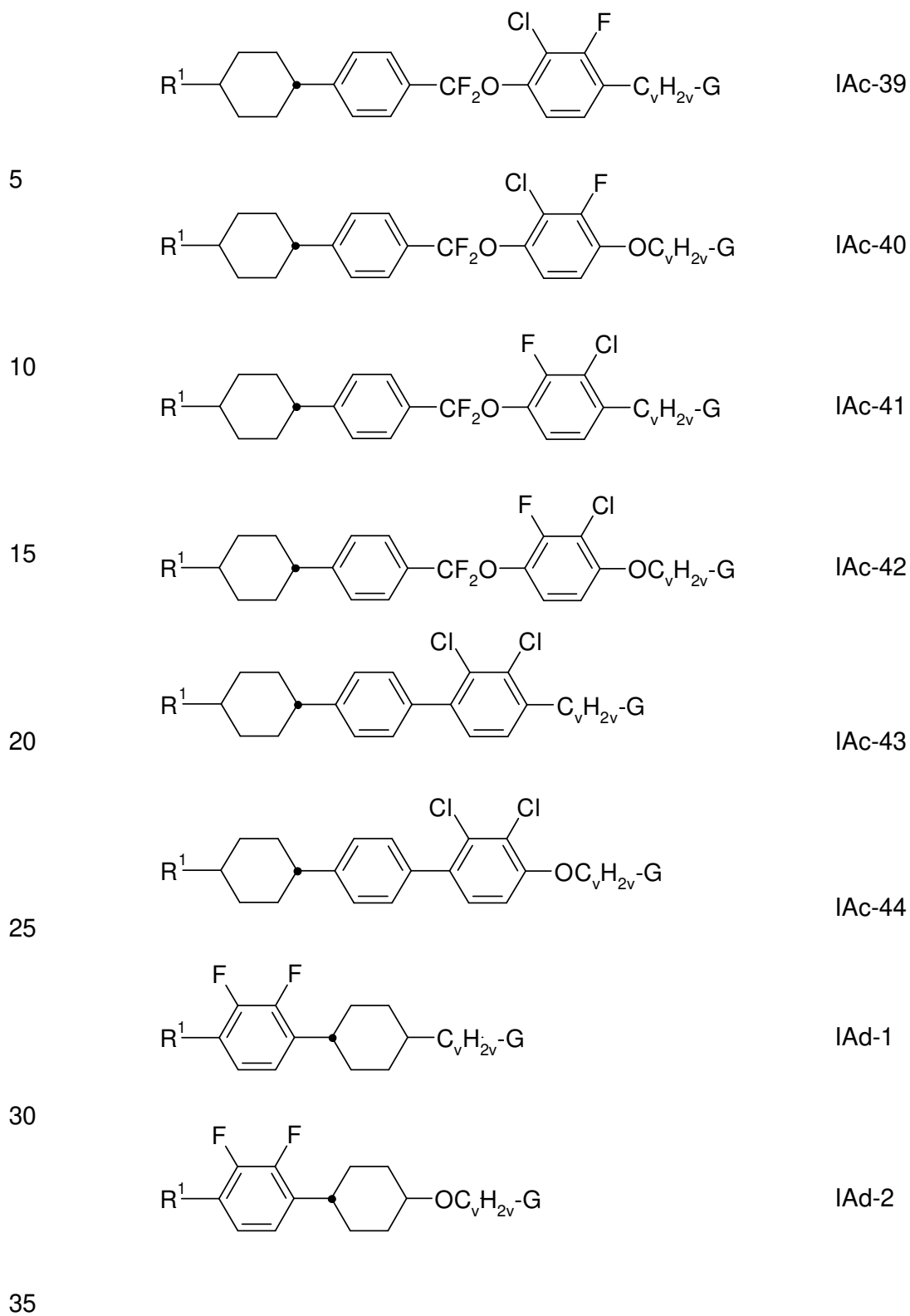


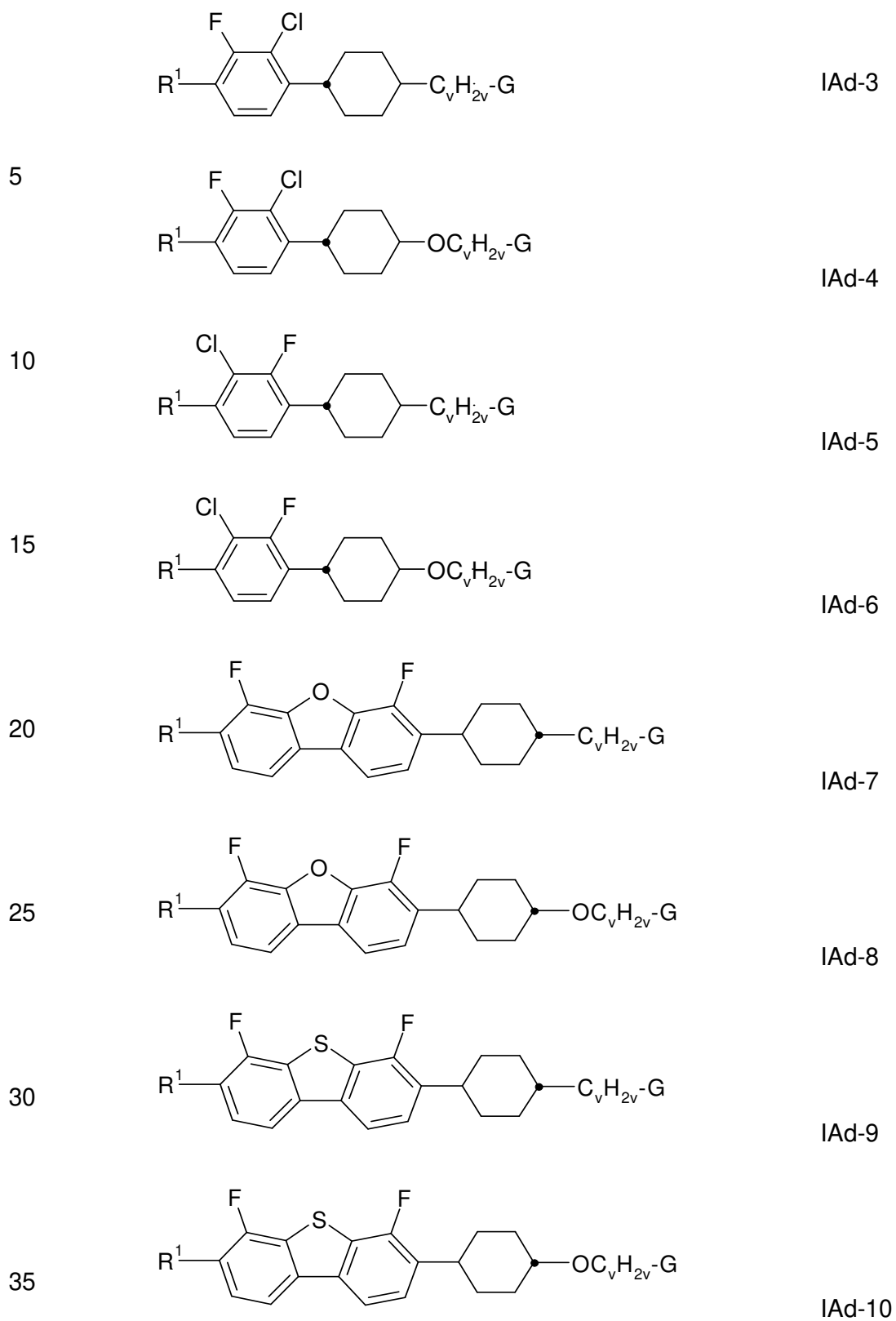


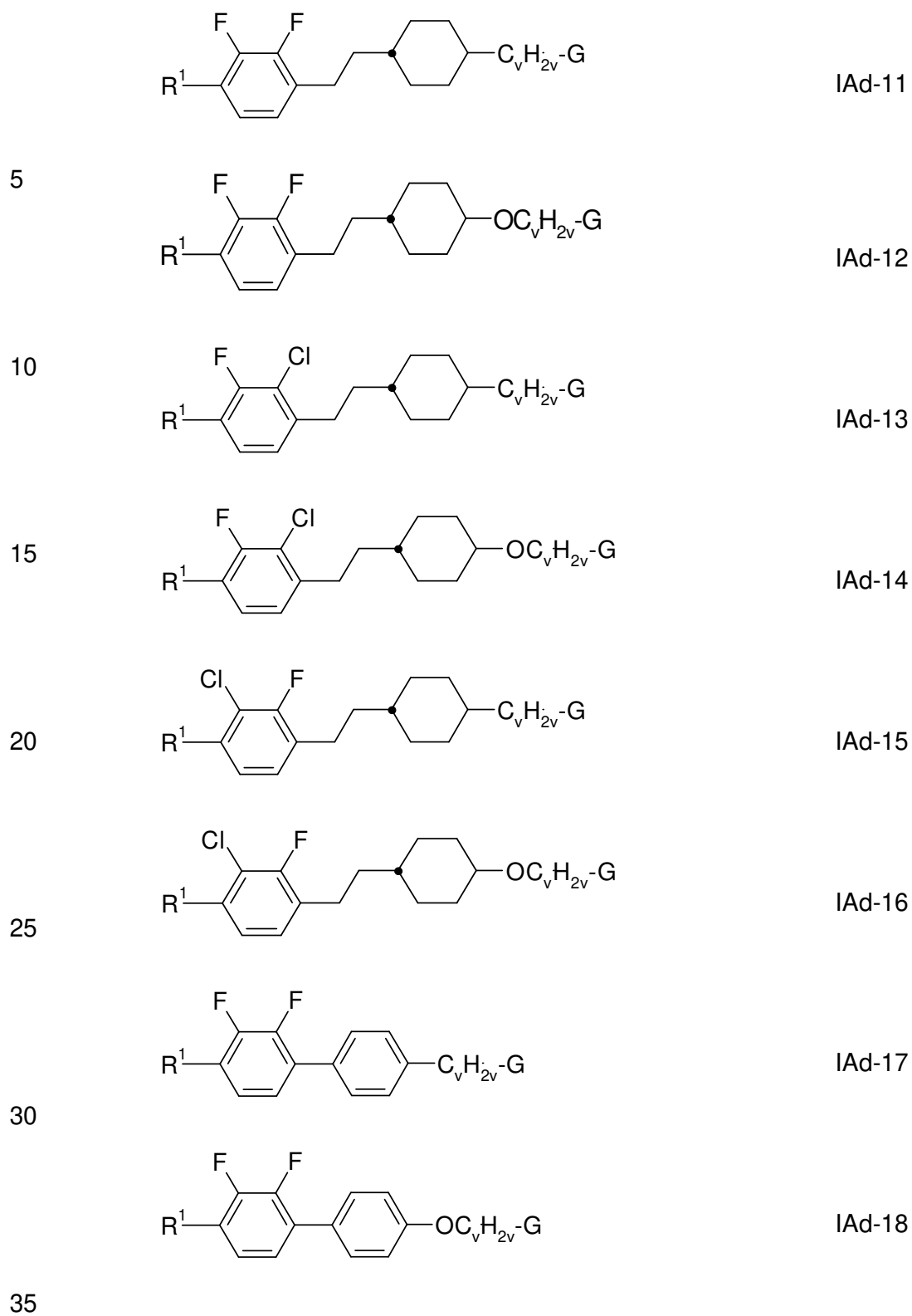


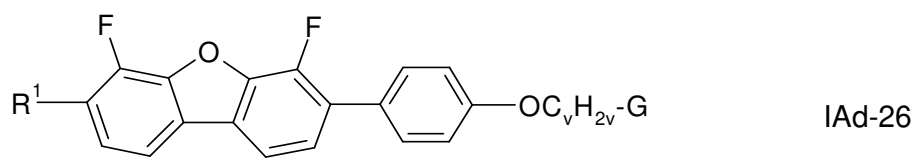
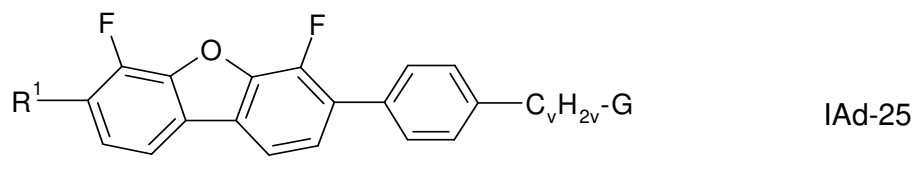
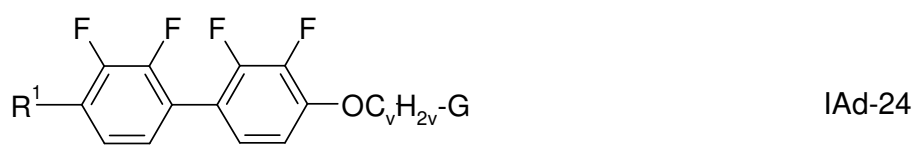
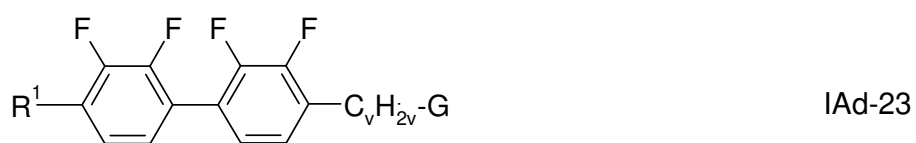
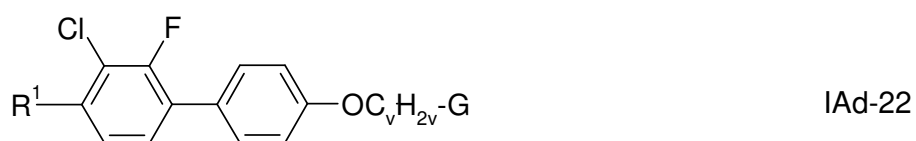
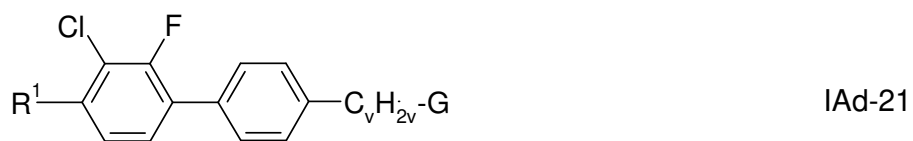
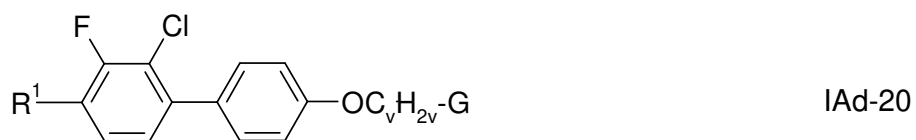
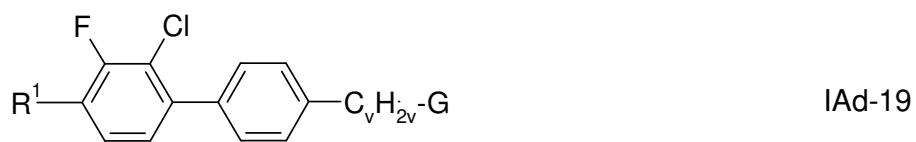


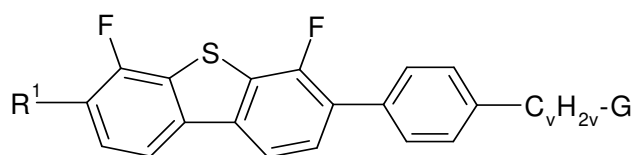






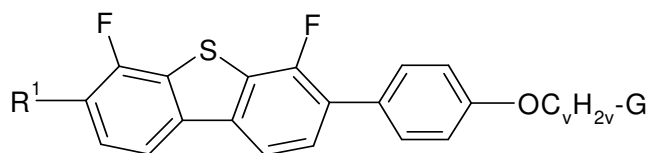






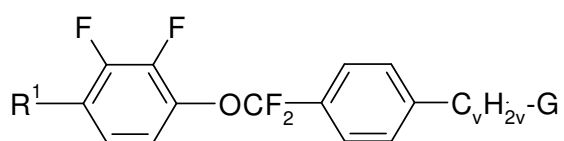
IAd-27

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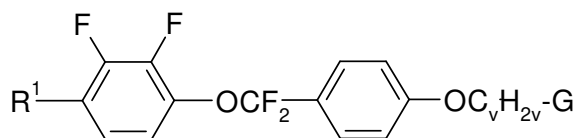
IAd-28

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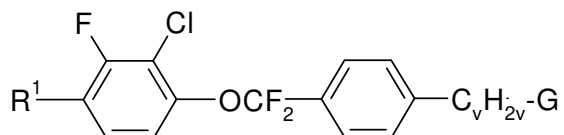
IAd-29

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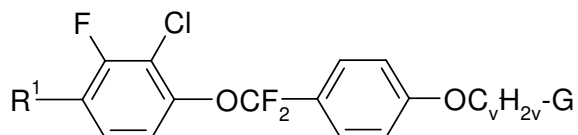
IAd-30

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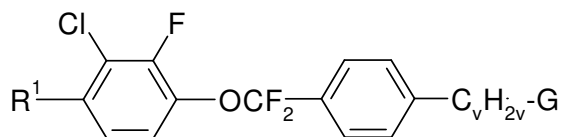
IAd-31

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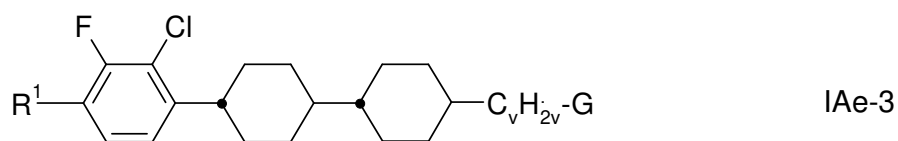
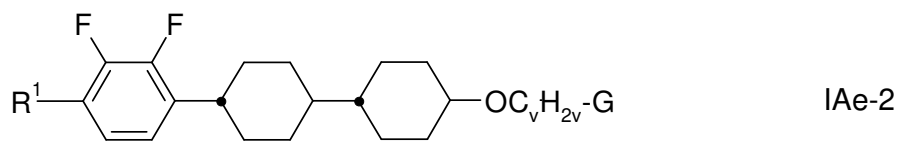
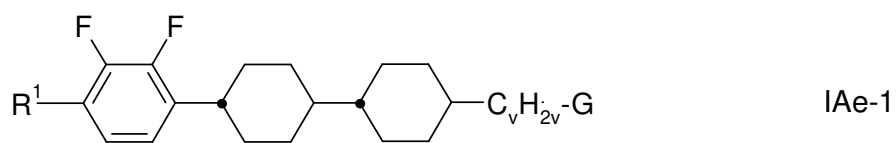
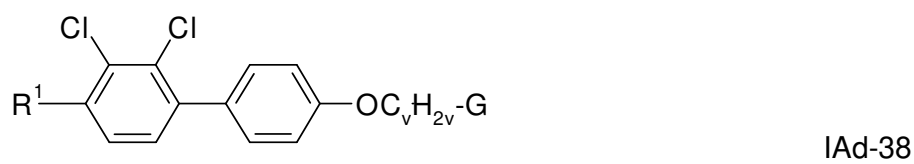
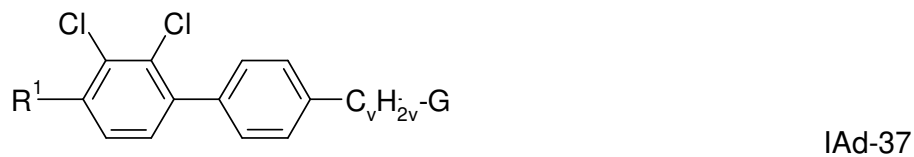
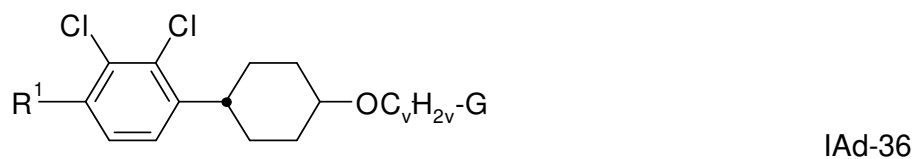
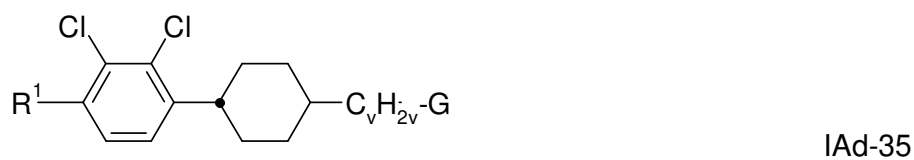
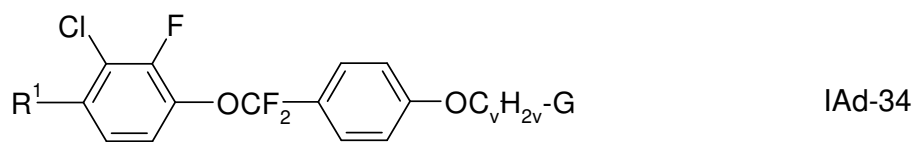
IAd-32

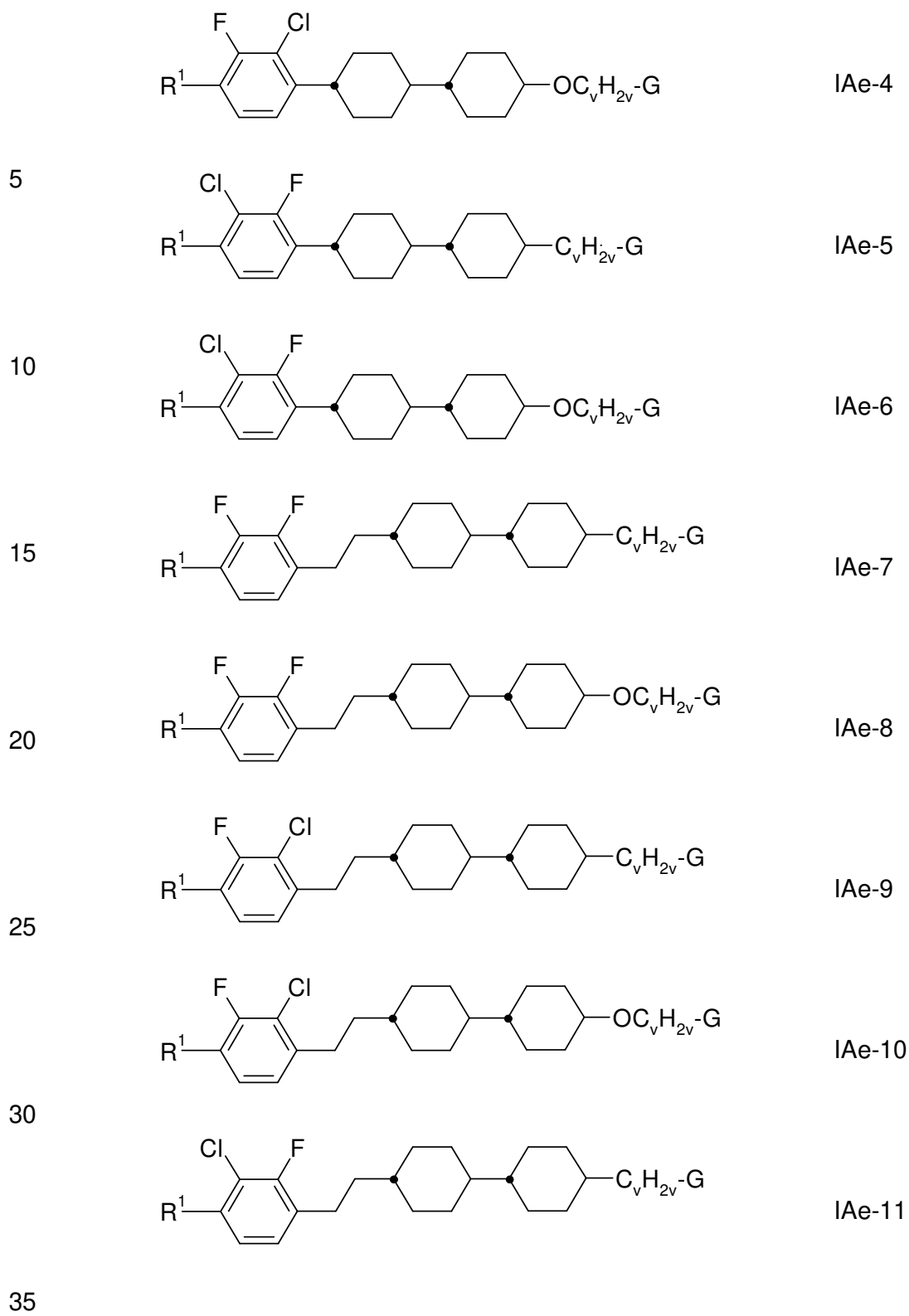
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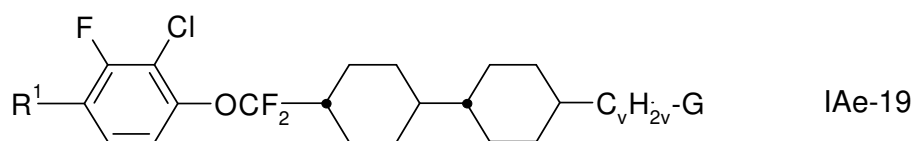
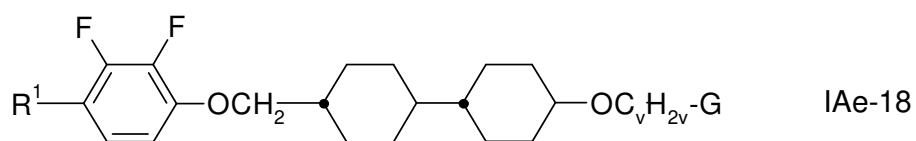
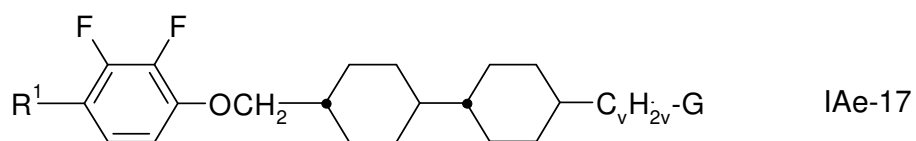
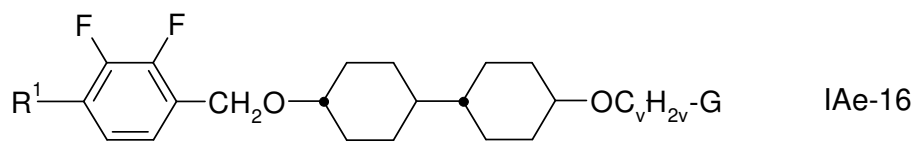
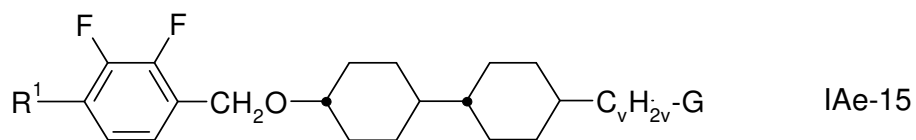
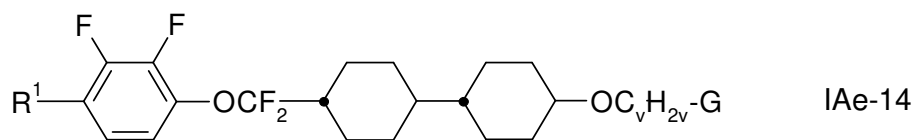
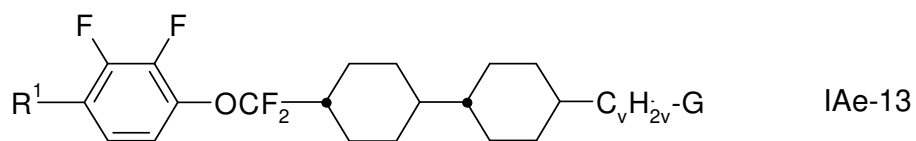
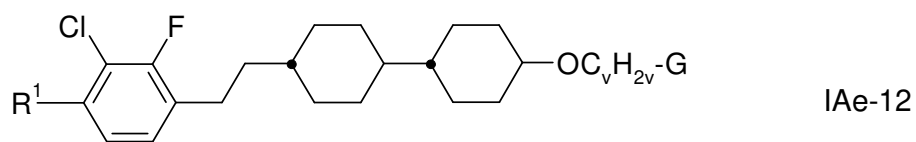


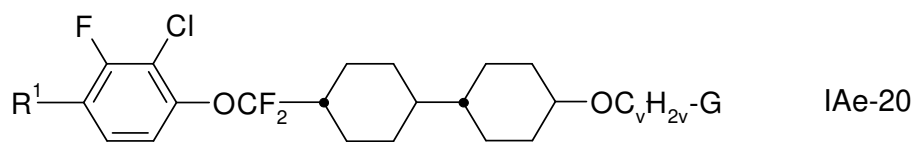
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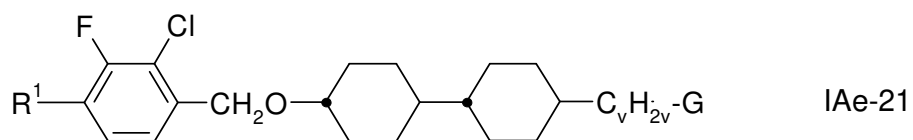




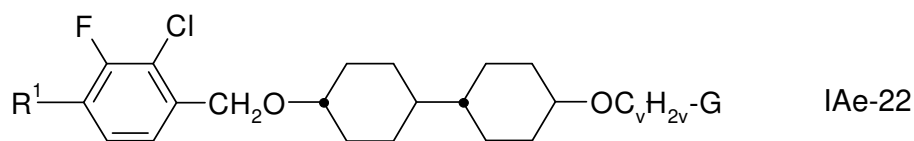




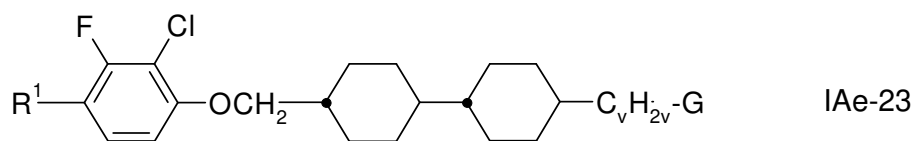
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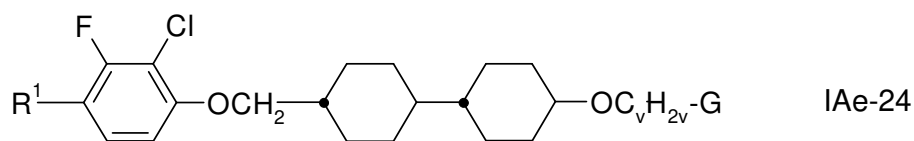
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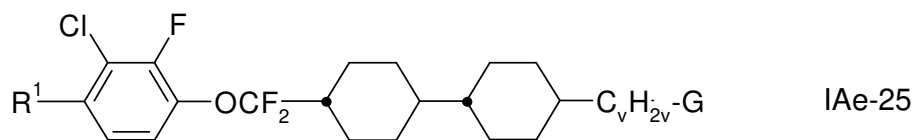
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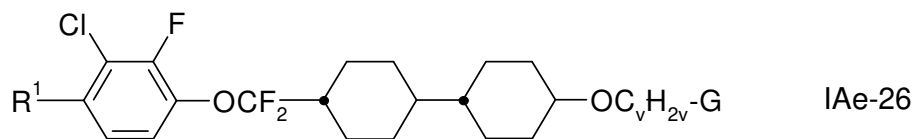
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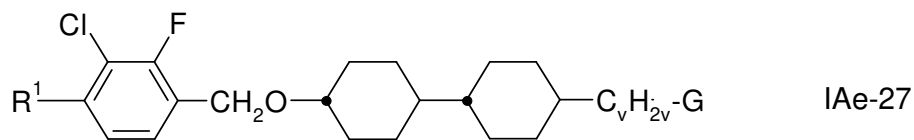
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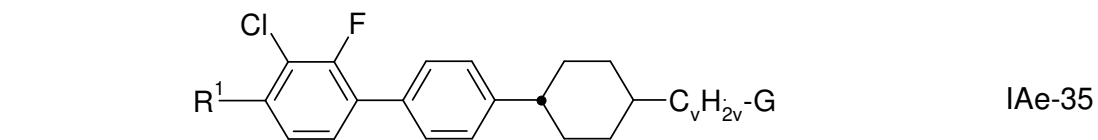
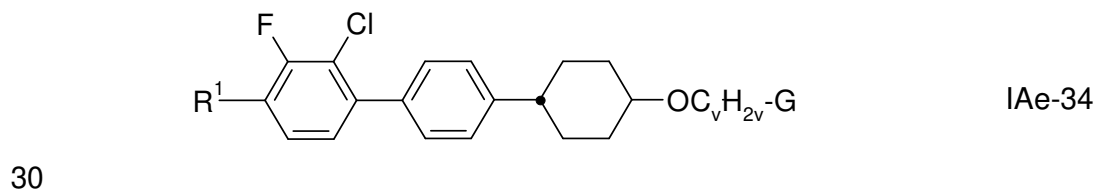
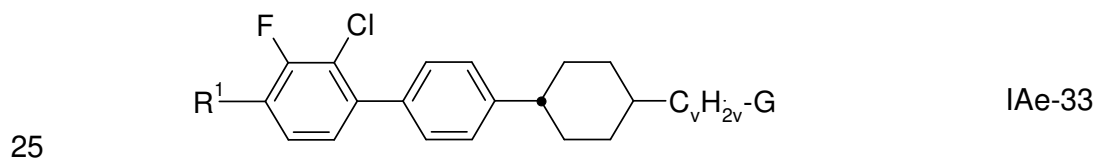
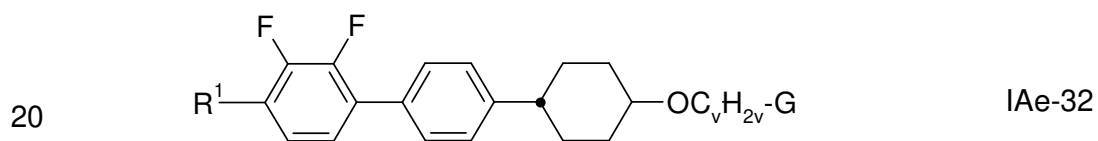
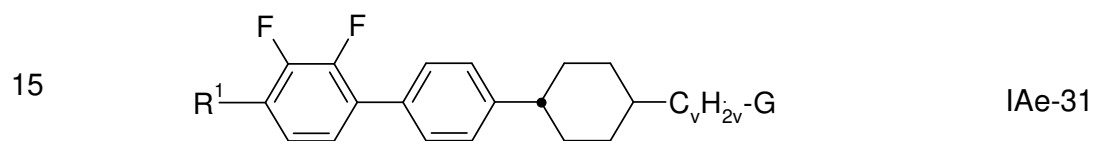
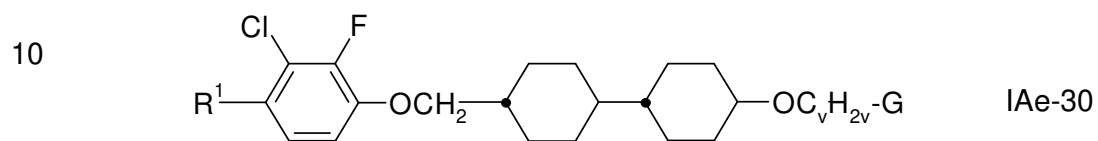
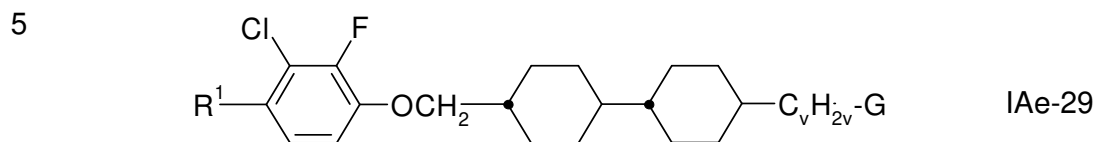
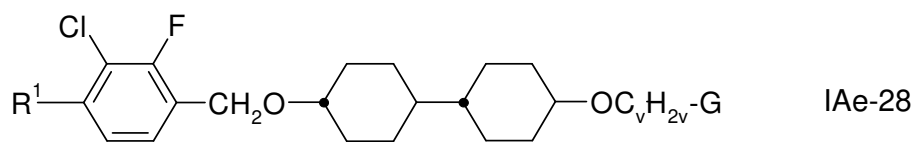


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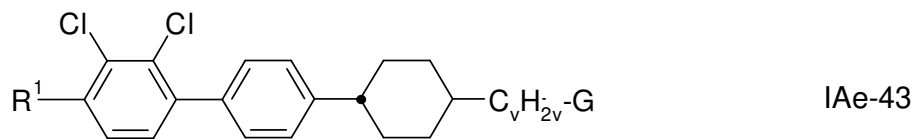
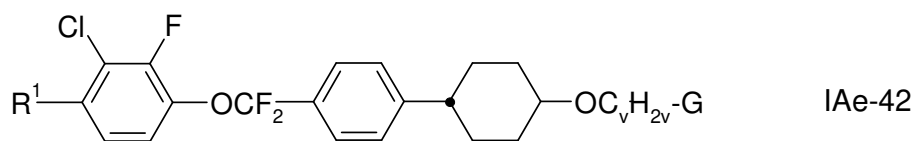
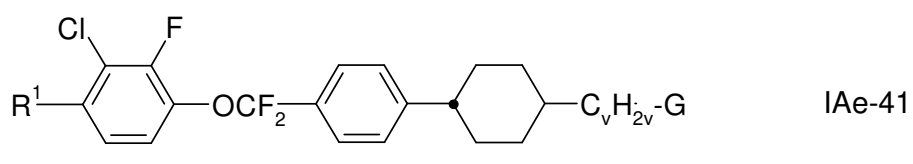
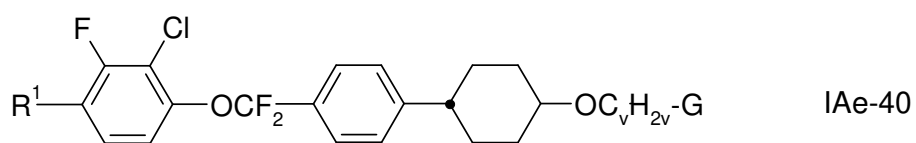
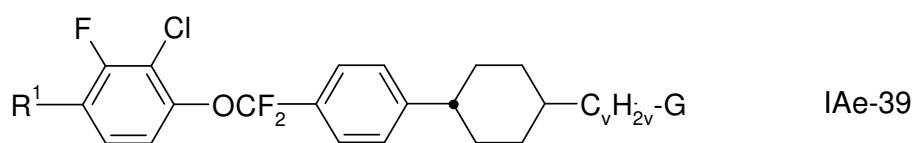
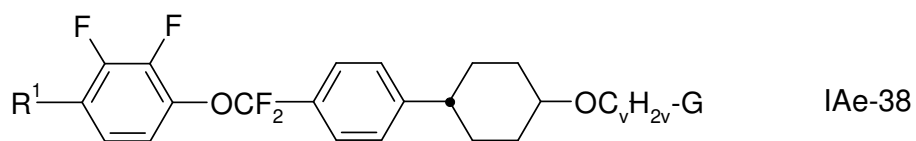
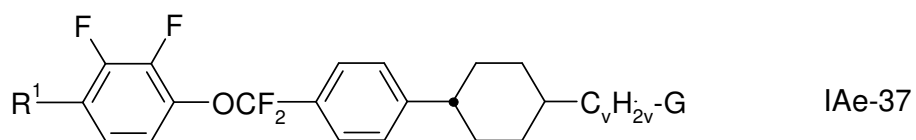
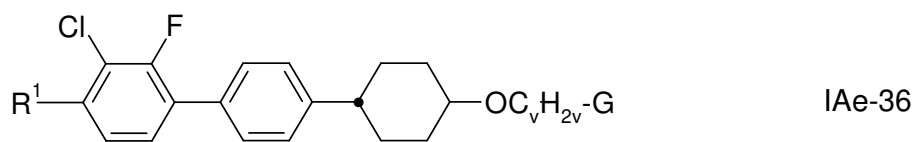


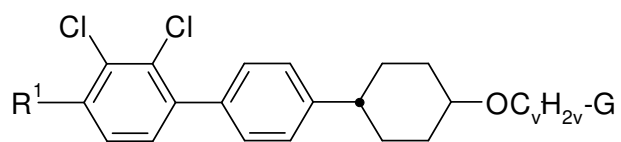
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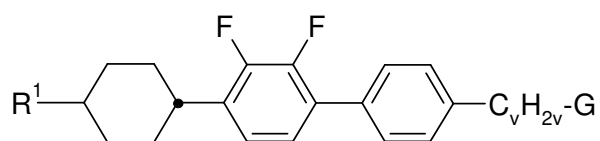
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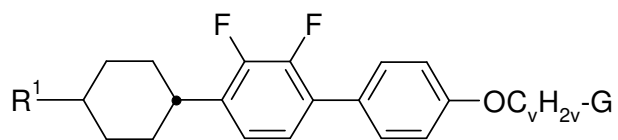
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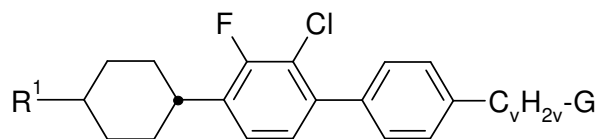
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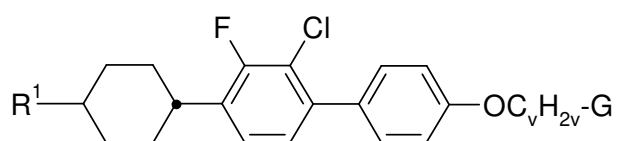
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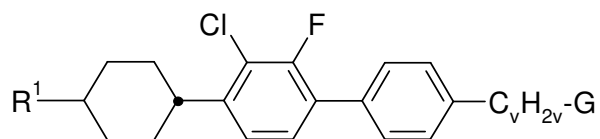
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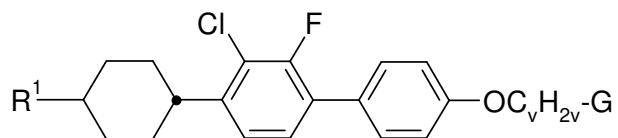
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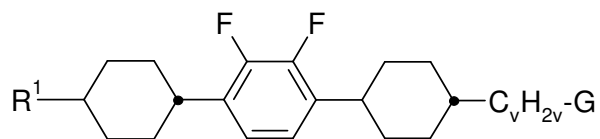


IAf-5

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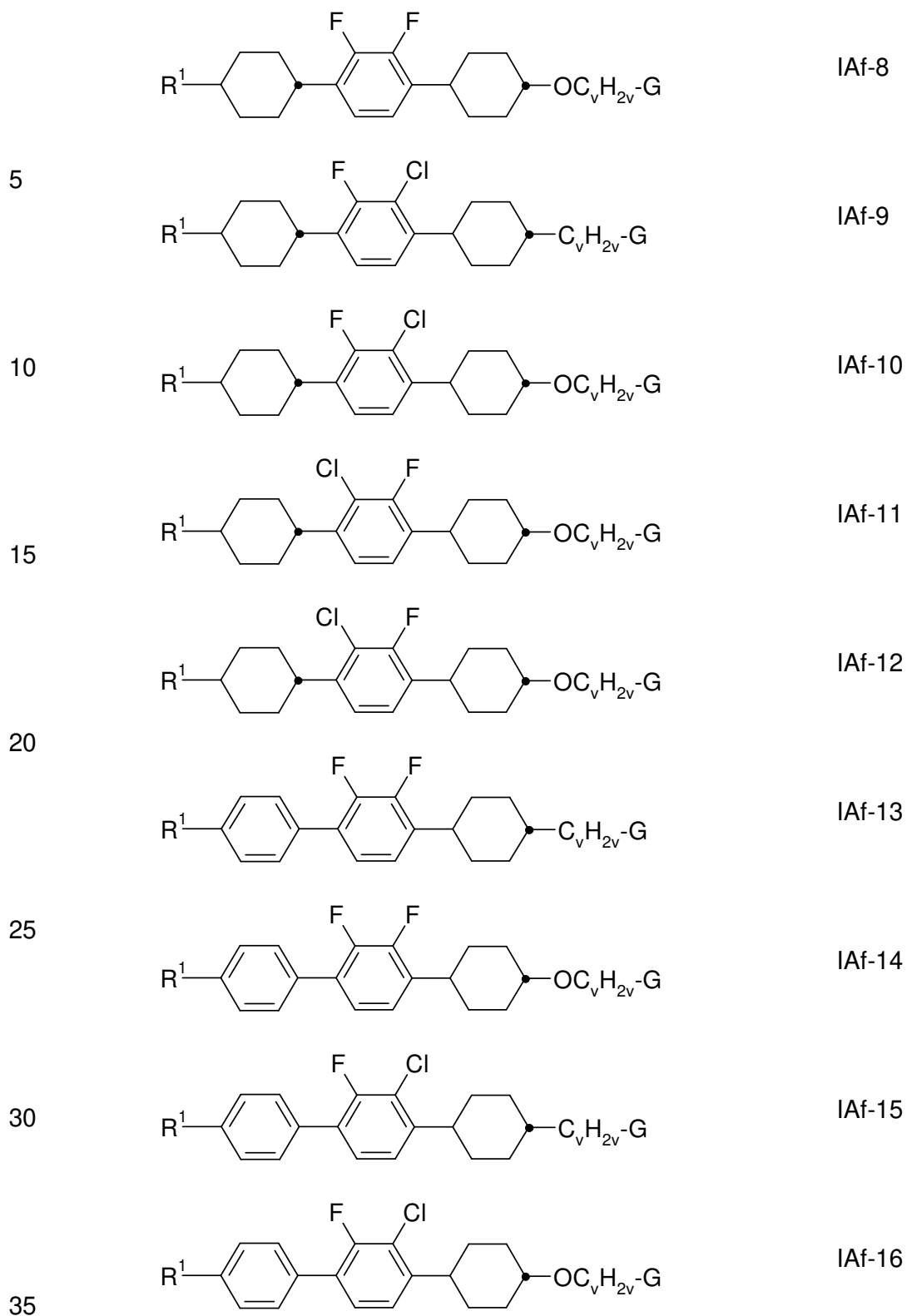


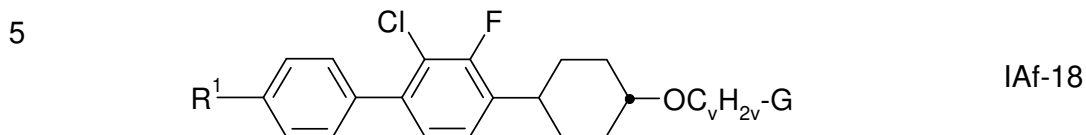
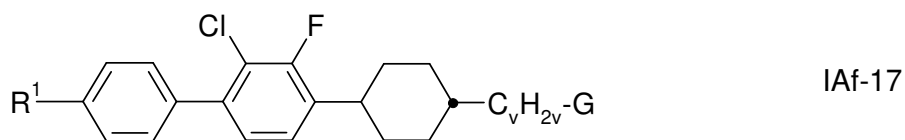
IAf-6



IAf-7

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in which R¹ and G have the meanings given above and preferably

10 R¹ denotes alkyl having 1 to 7 C atoms,

G denotes -SO₂OR^V or -PO(OR^V)₂,

15 R^V denotes an isopropyl or tert-butyl radical, and

v denotes an integer from 1 to 12, preferably from 2 to 7.

20 Also covered by the description are compounds of the formula IA in which the group -C_vH_{2v}- has been replaced by -C_vF_{2v}- in the sub-formulae IAa-1 to IAa-14, IAb-1 to IAb-34, IAc-1 to IAc-44, IAd-1 to IAd-38, IAe-1 to IAe-44 and IAf-1 to IAf-18.

25 The process according to the invention is particularly suitable for the production of molecular layers in which the molecules contain reactive groups which, as described below, can be chemically activated for use in atomic layer deposition (ALD) and subsequent metallisation.

30 Self-assembled monolayers (SAMs) are frequently used in CMOS technology for the selective passivation of surfaces against the deposition of other materials by ALD, as described in M. Hashemi, F. Sadat, B. R. Birchansky, S. F. Bent, ACS Appl. Mater. Interfaces 2016, 8, 33264–33272. It is desirable to be able to reactivate an SAM-passivated surface of this type in a

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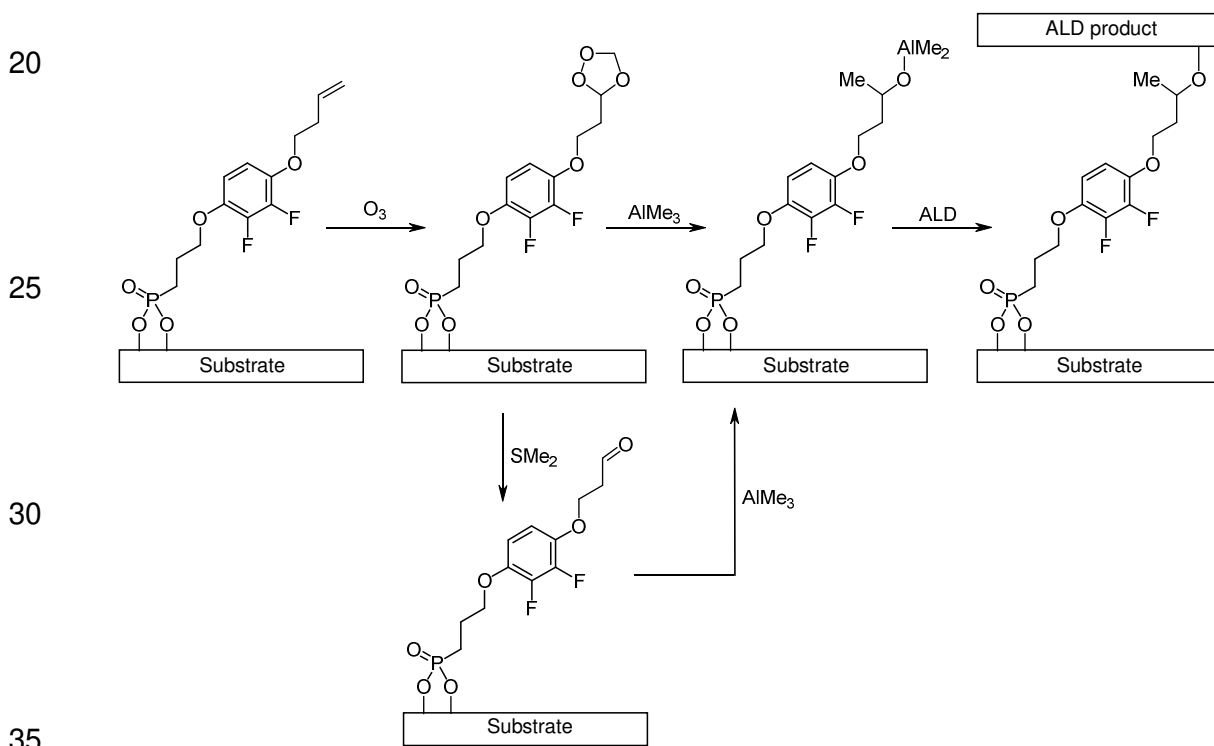
later process step in order to facilitate or simplify ALD deposition on the SAM. In particular for SAM-based electrically switchable tunnel junctions, a very useful process is one which facilitates the formation of a buffer layer under mild ALD conditions in order to protect the sensitive organic compounds of the SAM against high temperatures and reactive reagents during subsequent metal deposition on the SAM surface. The deposition of metal layers directly onto an SAM is only possible with very few metals, which, in addition, are often unsuitable for reliable and readily reproducible production of electronic components. An example is lead, which is deposited onto an SAM by vapour deposition. Typical problems are thermal damage to the sensitive SAM and migration of the top electrode metal through the SAM and reaction with the bottom electrode material. The use of a thin oxide or nitride layer deposited by ALD on the SAM protects the sensitive organic substances, acts as barrier layer and provides a nucleation layer for material deposition processes of all types.

A surface derivatised by an SAM allows ALD of, for example, aluminium oxide and other oxides only at very high concentrations or partial pressures of the starting substances (cf. S. Seo, B.C. Yeo, S.S. Han, C.M. Yoon, J.Y. Yang, J. Yoon, C. Yoo, H.-J. Kim, Y.-B. Lee, S.J. Lee et al., ACS Appl. Mater. Interfaces, 2017). Such high partial pressures may be hazardous (for example with highly flammable trimethylaluminium as process gas) and reduce the advantage of the chemoselectivity of the monolayer compared with other surfaces in respect of area-selective deposition. The molecular layer is therefore used firstly as ALD inhibitor, as described here, with subsequent activation facilitating ALD under normal process conditions. A preferred reactive group for the derivatisation of a SAM is the alkenyl group. Alkenyl-terminated SAMs and SAM precursors are known in principle, as described, for example, in M. C. Campos, J. M. J. Paulusse, H. Zuilhof, Chem. Comm. 2010, 46, 5512–5514, or are even commercially available, such as, for example, allyltrichlorosilane (CAS No. 107-37-9) and 10-undecenylphosphonic acid (CAS No. 867258-92-2).

The activation of the SAM containing alkenyl groups is carried out, for example, using ozone by the method of T. M. McIntire, O. Ryder, B. J. Finlayson-Pitts, J. Phys. Chem. C 2009, 113, 11060–11065, for the generation of a secondary ozonide, which is derivatised by subsequent treatment with trimethylaluminium in the gas phase by the method of J. Huang, M. Lee, A. Lucero and J. Kim, Chem. Vap. Deposition 2013, 19, 142–148.

The ozonide can also be reduced via an intermediate step, for example to aldehydes, using suitable volatile reducing agents (alkyl sulfides or alkylphosphines) whose oxides are likewise volatile (example dialkyl sulfone, trialkylphosphine oxide) (see Scheme 1). The reactions are depicted in Scheme 1 below.

Scheme 1



Oxides, such as Al_2O_3 , TiO_2 , ZrO_2 , HfO_2 , ITO, AZO, IGZO or IGO, nitrides (TiN_x , TaN_x or Si_3N_4), or metals, such as W, Mo, Co, Cr, Al, Cu, Ag or Ru, can be deposited on the oxidatively activated SAM by ALD (Scheme 1: “ALD product”).

5

A further layer can subsequently be applied to the layer deposited onto the SAM by ALD is subsequently possible. In this case, a metal or another conducting or semiconducting material is applied. Preferred methods for the application of this further layer are physical gas-phase deposition (vapour deposition, sputtering, etc.), chemical gas-phase deposition, and ALD.

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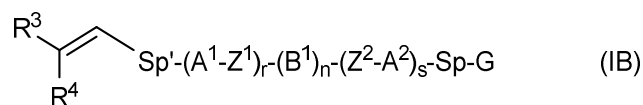
According to a further aspect of the present invention, a process is thus provided which comprises the following steps:

- (1) provision of a substrate having a substrate surface,
- (2) application of a solution comprising one or more compounds of the formula IB onto the substrate surface,
- (3) heating of the substrate to a temperature in the range from 60°C to 300°C ,
- (4) treatment of the surface with ozone,

20

25

where formula IB is defined as follows:



30

in which

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- group II-VI semiconductors, in particular ZnO, ZnS, ZnSe, ZnTe, CdS, CdSe, CdTe, $\text{Hg}_{(1-x)}\text{Cd}_x\text{Te}$, BeSe, BeTe_x and HgS;
- group III-VI semiconductors, in particular GaS, GaSe, GaTe, InS, InSe_x and InTe,
- 5 - group I-III-VI semiconductors, in particular CuInSe_2 , CuInGaSe_2 , CuInS_2 and CuInGaS_2 ,
- group IV-IV semiconductors, in particular SiC and SiGe,
- group IV-VI semiconductors, in particular SeTe;
- 10
- organic semiconductors, in particular polythiophene, tetracene, pentacene, phthalocyanines, PTCDA, MePTCDI, quinacridone, acridone, indanthrone, flaranthrone, perinone, AlQ_3 , and mixed systems, in particular PEDOT:PSS and polyvinylcarbazole/TLNQ complexes;
- 15
- metals, in particular Ta, Ti, Co, Mo, Pt, Ru, Au, Ag, Cu, Al, W and Mg;
- conductive oxidic materials, in particular indium tin oxide (ITO), indium gallium oxide (IGO), $\text{InGa-}\alpha\text{-ZnO}$ (IGZO), aluminium-doped zinc oxide (AZO), tin-doped zinc oxide (TZO), fluorine-doped tin oxide (FTO) and antimony tin oxide;
- 20
- metal oxides (SiO_2 , Al_2O_3 , TiO_2 , HfO_2 and ZrO_2);
- metal nitrides (Si_3N_4 , TaN_x and TiN_x);
- 25
- mixed metal oxynitrides (TiN_xO_y and TaN_xO_y).
- 30

In an alternative embodiment, the substrate surface has a coating consisting of a different material from the substrate. The thickness of the layer is preferably 0.5 - 5 nm. Methods for the production of such layers are known to the person skilled in the art, preference being given to methods such as atomic layer deposition, chemical gas-phase deposition or treatment with

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oxidative or reductive plasma, preferably with oxygen plasma. The coating is suitable for the formation of a particularly stable self-assembled monolayer, and preferably consists of an oxide and/or nitride of one or more metals or semi-metals, particularly preferably of SiO_2 , Al_2O_3 , HfO_2 , TiO_2 , TiN_x or TiN_xO_y .

In the process according to the invention, the application of the solution of the material to the substrate can be carried out by conventional methods for the coating of surfaces, such as dip coating, knife coating, spray coating, roller coating, spin coating, furthermore spray coating, slot-die coating, and conventional printing processes, such as, for example, ink-jet printing, screen printing, microcontact stamp printing, and in addition by deposition from the gas phase. Spin coating and deposition from the gas phase are preferred.

After the application of the solution, the solvent is firstly removed, for example by warming to a temperature above 20°C and/or under reduced pressure below 1000 hPa, preferably below 750 hPa, and/or under a stream of inert gas. The substrate is subsequently heated to a temperature in the range from 60°C to 300°C , preferably from 100°C to 250°C , particularly preferably from 140°C to 180°C . Without being tied to a theory, it is thought that the secondary or tertiary esters of the formula I eliminate an alkene on heating and are then in the form of the free acids, which then bind to the substrate by chemisorption, in particular by an addition reaction or condensation reaction.

The component is then cleaned from reaction products and excess material by washing with a suitable solvent, for example isopropanol or tetrahydrofuran, optionally under the action of ultrasound, and dried again as described above.

In a preferred embodiment, the substrate is annealed after the deposition of the monolayer. The annealing is carried out at a temperature above

20°C and below 300°C, preferably above 50°C and below 200°C, particularly preferably above 90°C and below 150°C. The duration of the annealing is 10 min to 48 h, preferably 1 to 24 h, particularly preferably 4 to 16 h.

5 In an alternative embodiment, the deposition of the material is carried out from the gas phase at a pressure of less than 500 hPa, preferably less than 200 hPa, particularly preferably less than 50 hPa. The material is evaporated here at a temperature at which decomposition does not occur.
10 The determination this temperature is known to the person skilled in the art, a suitable method being, for example, dynamic differential calorimetry.

The compounds of the general formula I can be prepared by methods
15 known per se, as described in the literature (for example in the standard works, such as Houben-Weyl, Methoden der organischen Chemie [Methods of Organic Chemistry], Georg-Thieme-Verlag, Stuttgart), to be precise under reaction conditions which are known and suitable for the said reactions. Use can be made here of variants known per se which are not men-
20 tioned here in greater detail.

If desired, the starting materials can also be formed in situ by not isolating them from the reaction mixture, but instead immediately converting them
25 further into the compounds of the general formula I.

The syntheses of compounds of the general formula I according to the invention are described in illustrative terms in the examples. The starting
30 substances can be obtained by generally accessible literature procedures or are commercially available.

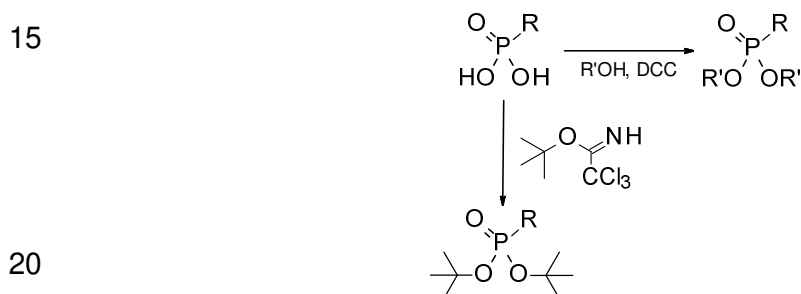
Particularly suitable synthetic routes to the compounds according to the invention are illustrated below with reference to Schemes 1 and 2 and are
35 explained in greater detail with reference to the working examples, without restricting them thereby.

Phosphonic acid esters of the formula I can be prepared from the corresponding phosphonic acids by standard processes (Schemes 1 and 2).

This is carried out, for example, by the method of A. K. Purohit, D.

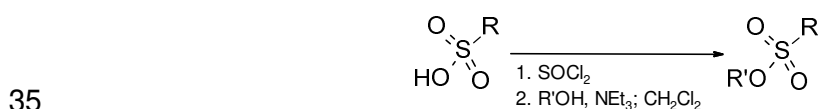
5 Pardasani, V. Tak, A. Kumar, R. Jain, D. K. Dubey, *Tetrahedron Lett.* **2012**, 53, 3795-3797, from the acid and the alcohol in the presence of a suitable condensation reagent, such as polymer-bound triphenylphosphine/iodine, or by the method of T. Hara, S. R. Durell, M. C. Myers, D. H. Appella, *J.*
10 *Am. Chem. Soc.* **2006**, 128, 1995-2004, from the acid by reaction with an activated alcohol, such as tert-butyl trichloroacetimidate

Scheme 1:



Sulfonic acid esters of the formula I are prepared via the acid chloride by
25 reaction with an alcohol in the presence of a base, for example triethylamine, as described, for example, in Z. Guan, X. Chai, S. Yu, Q. Meng, Q. Wu, *Chem. Biol. Drug Des.* **2010**, 76, 496-504. Another process, in particular for the preparation of secondary alkyl sulphonates, is, according to I.
Galyker, W. C. Still, *Tetrahedron Lett.* **1982**, 23, 4461-4464, the Mitsunobu
30 condensation.

Scheme 2:



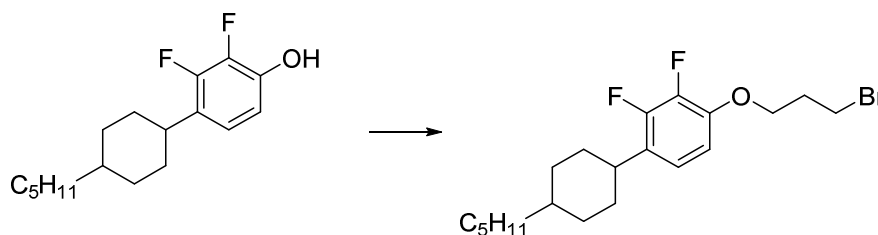
The invention is not restricted to the illustrative embodiments described here and the aspects emphasised therein. Instead, a multiplicity of modifications which are within the scope of action of the person skilled in the art are possible within the range indicated by the claims.

Examples

1. Synthesis examples

Example 1: Di-tert-butyl (3-(2,3-difluoro-4-(4-pentylcyclohexyl)phenoxy)propyl)phosphonate

Step 1: 1-(3-Bromopropoxy)-2,3-difluoro-4-(4-pentylcyclohexyl)benzene



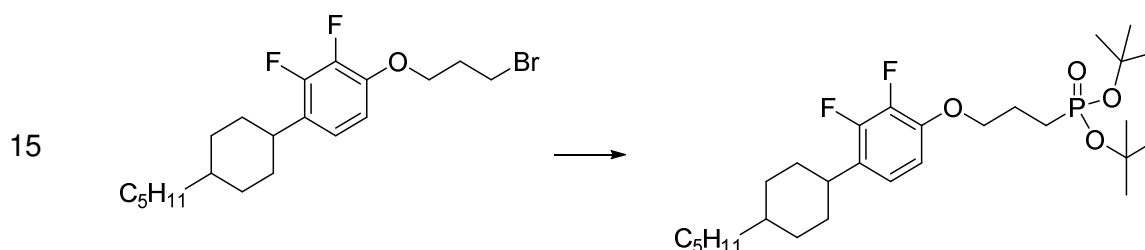
2,3-Difluoro-4-(4-pentylcyclohexyl)phenol (7.6 g, 27 mmol) is dissolved in acetone (80 ml), anhydrous potassium carbonate (20.0 g, 150 mmol) and 1,3-dibromopropane (20.4 g, 10.4 ml, 105 mmol) are added, and the mixture is heated under reflux for 12 h. The batch is filtered and evaporated, and the residue is chromatographed on silica gel with dichloromethane:*n*-pentane (1:10), giving 1-(3-bromopropoxy)-2,3-difluoro-4-(4-pentylcyclohexyl)benzene as a colourless solid of m.p. 40–43°C.

¹H NMR (400 MHz, CDCl₃): δ 6.83 (dd, ³J_{HH} = 9.2 Hz, ⁴J_{HF} = 2.3 Hz, 1H, H_{Ar}), 6.68 (dd, ³J_{HH} = 7.33 Hz, ⁴J_{HF} = 1.9 Hz, 1H, H_{Ar}), 4.13 (t, ³J_{HH} = 5.7 Hz, 2H, CH₂), 3.59 (t, ³J_{HH} = 6.1 Hz, 2H, CH₂), 2.98 (tt, ³J_{HH} = 12.1 Hz, ⁴J_{HH} = 2.9 Hz, 1H, CH), 2.31 (q, ³J_{HH} = 5.9 Hz, 2H, CH₂), 1.88 – 1.78 (m,

4H, CH₂, CH), 1.46 – 1.36 (m, 2H, CH₂), 1.35 – 1.17 (m, 2H, CH₂), 1.09 – 0.99 (m, 9H, CH₂), 0.86 (t, ³J_{HH} = 7.3 Hz, 3H, CH₃)

¹³C NMR (101 MHz, CDCl₃): δ 149.0 (dd, ¹J_{CF} = 245.1 Hz, ³J_{CF} = 10.2 Hz), 145.6 (dd, ³J_{CF} = 8.2 Hz, ⁴J_{CF} = 2.9 Hz), 141.0 (dd, ¹J_{CF} = 246.9 Hz, ³J_{CF} = 15.3 Hz), 128.2 (dd, ²J_{CF} = 12.5 Hz, ³J_{CF} = 1.3 Hz), 120.3 (dd, ²J_{CF} = 5.7 Hz, ³J_{CF} = 4.6 Hz), 109.2 (d, ²J_{CF} = 3.3 Hz), 67.1 (s), 40.1 (s), 36.7 (s), 33.3 (s), 33.1 (s), 32.4 (s), 31.7 (s), 31.5 (s), 27.7 (s), 23.4 (s), 14.1 (s).

Step 2: Di-tert-butyl (3-(2,3-difluoro-4-(4-pentylcyclohexyl)phenoxy)propyl)-phosphonate



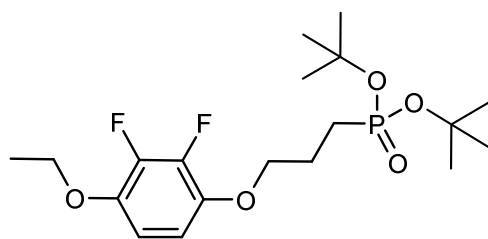
Sodium hydride (0.3 g, 7.0 mmol, 60% in mineral oil) is added in portions to a solution of di-*tert*-butyl phosphite (1.2 g, 1.3 ml, 6.4 mmol) in anhydrous tetrahydrofuran (THF, 50 ml) under argon. When the evolution of gas is complete, a solution of 1-(3-bromopropoxy)-2,3-difluoro-4-(4-pentylcyclohexyl)benzene (2.5 g, 6.2 mmol in 2 ml THF) is added, and the batch is left to stir at room temp. for 12 h. After aqueous work-up, the mixture is extracted with ether, the combined org. phases are dried over sodium sulfate and evaporated, and the crude product is chromatographed on silica gel with ethyl acetate, giving di-*tert*-butyl (3-(2,3-difluoro-4-(4-pentylcyclohexyl)phenoxy)propyl)phosphonate as a colourless solid of m.p. 47°C, decomposition point 149°C.

¹H NMR (400 MHz, CDCl₃): δ 6.77 (dd, ³J_{HH} = 9.2 Hz, ⁴J_{HF} = 2.3 Hz, 1H, H_{ar}), 6.61 (dd, ³J_{HH} = 7.33 Hz, ⁴J_{HF} = 1.9 Hz, 1H, H_{ar}), 4.00 (t, ³J_{HH} = 6.1 Hz, 2H, CH₂) 2.56 (t, ³J_{HH} = 11.9 Hz, 1H, CH), 2.11 – 1.93 (m, 3H, CH₂, CH), 1.87 – 1.73 (m, 8H, CH₂), 1.43 (s, 18H, CH₃), 1.42 – 1.18 (m, 10H,

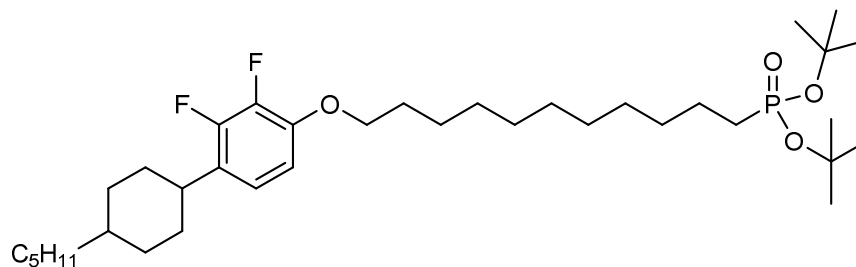
CH_2), 0.83 (t, $^3J_{HH} = 7.0$ Hz, 3H, CH_3); ^{19}F NMR (376 MHz, $CDCl_3$): δ -
 143.3 (dd, $^3J_{FF} = 19.6$ Hz, $^4J_{FH} = 7.4$ Hz, 1F, F_{ar}), -159.5 (dd, $^3J_{FF} =$
 18.0 Hz, $^4J_{FH} = 7.1$ Hz, 1F, F_{ar}); ^{31}P NMR (161 MHz, $CDCl_3$): δ 23.5 (s, 1P,
 5 $P(O)(OtBu)_2$); ^{13}C NMR (101 MHz, $CDCl_3$): δ 149.4 (dd, $^1J_{CF} = 245.1$ Hz,
 $^3J_{CF} = 10.2$ Hz), 146.0 (dd, $^3J_{CF} = 8.2$ Hz, $^4J_{CF} = 2.9$ Hz), 141.5 (dd, $^1J_{CF} =$
 246.9 Hz, $^3J_{CF} = 15.3$ Hz), 128.4 (dd, $^2J_{CF} = 12.5$ Hz, $^3J_{CF} = 1.3$ Hz), 120.5
 (dd, $^2J_{CF} = 5.7$ Hz, $^3J_{CF} = 4.6$ Hz), 109.5 (d, $^2J_{CF} = 3.3$ Hz), 81.6 (d, $^3J_{CP} =$
 8.6 Hz), 69.4 (d, $^2J_{CP} = 16.2$ Hz), 37.3 (s), 37.2 (s), 37.0 (s), 33.4 (s), 33.0
 10 (s), 32.2 (s), 30.4 (d, $^2J_{CP} = 3.9$ Hz), 30.3 (s), 26.6 (s), 26.5 (d, $^1J_{CP} =$
 147.1 Hz), 23.6 (d, $^2J_{CP} = 5.7$ Hz), 22.7 (s), 14.1 (s).

The following are prepared analogously to Example 1:

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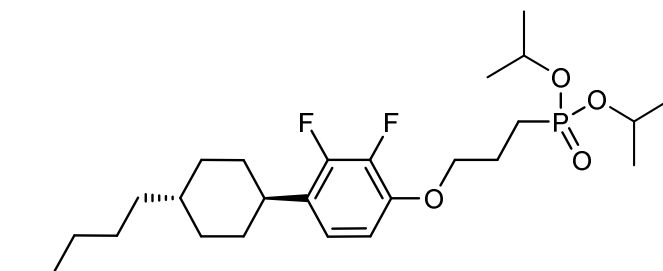


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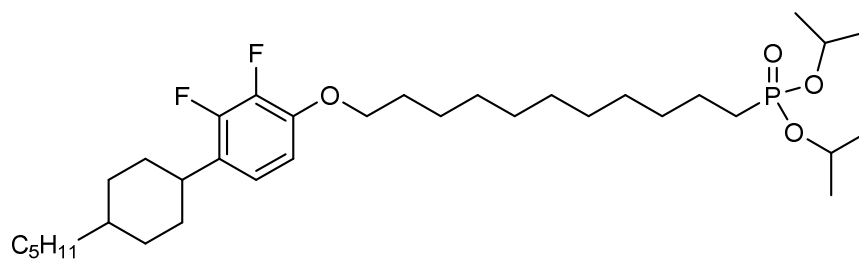
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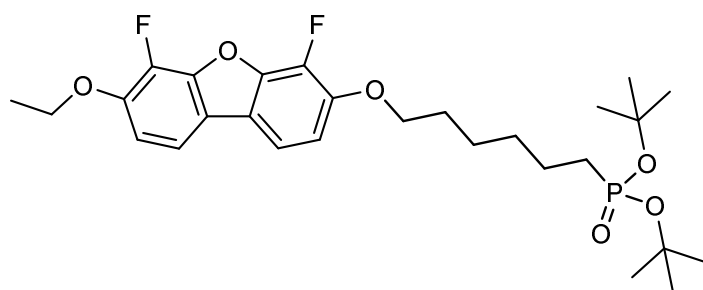


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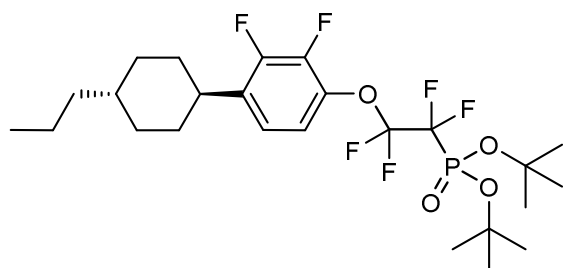
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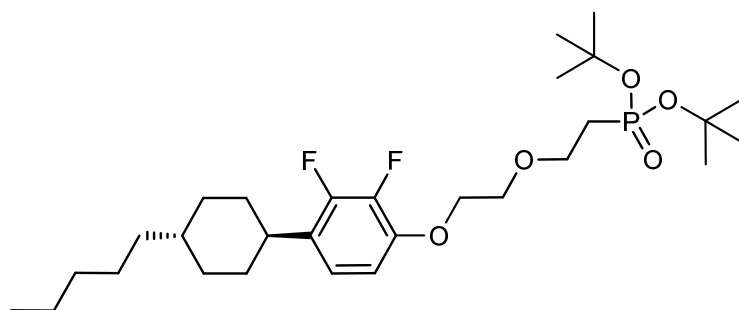
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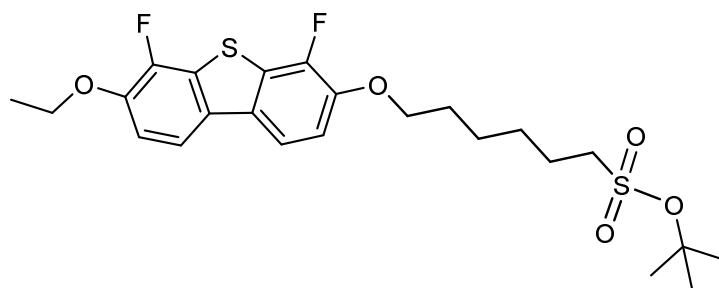
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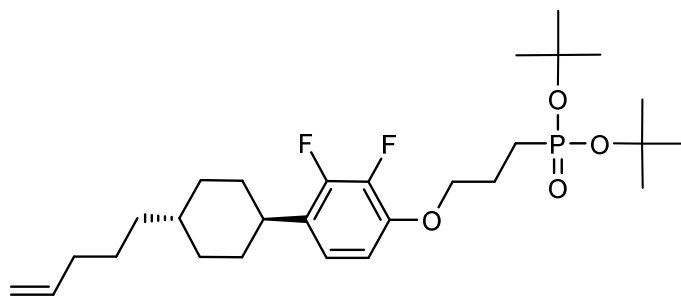
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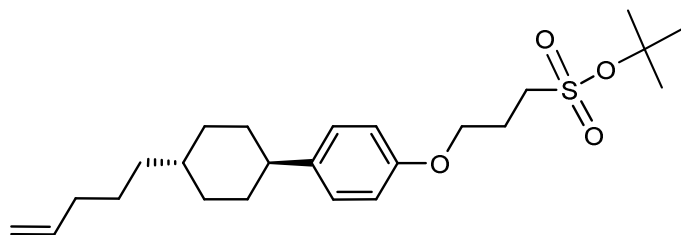
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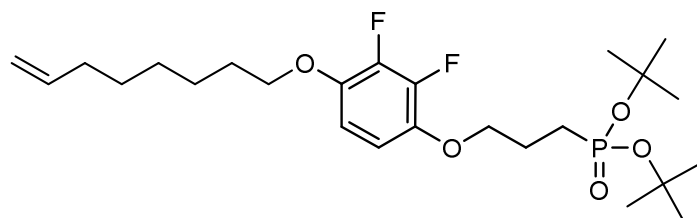
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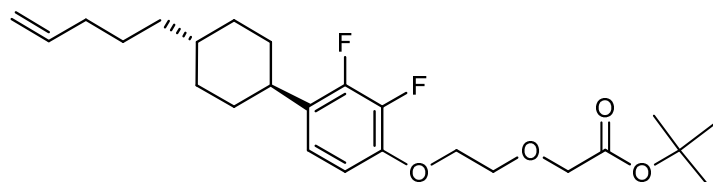
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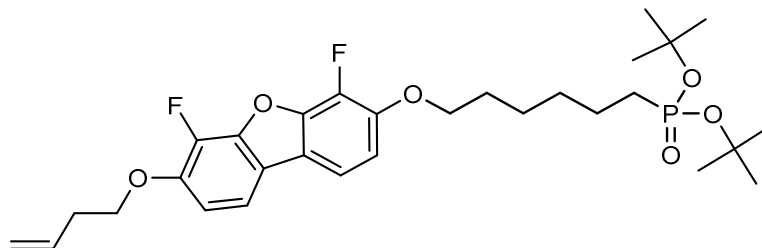
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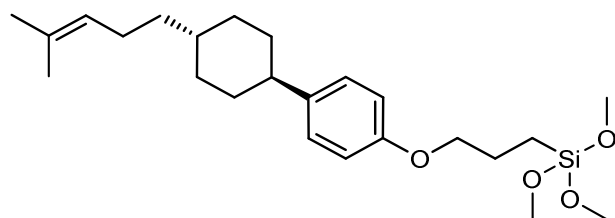
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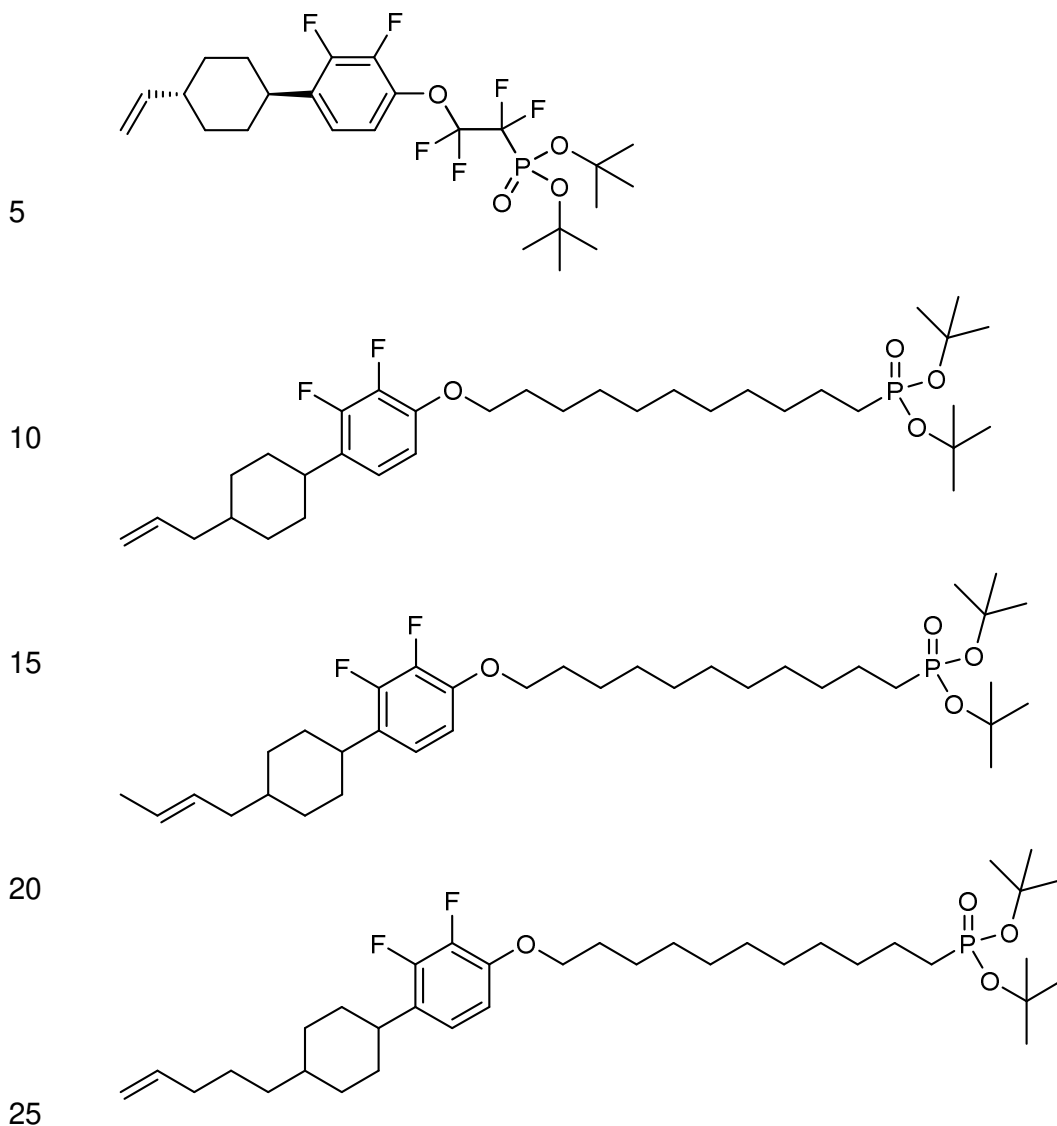
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Use examples

Preparation of an SAM by spin coating

30 Example 1: Preparation of an SAM on an Al_2O_3 substrate.

A 1-2 nm thick aluminium oxide layer is produced on a silicon wafer (8 x 8 mm, p^{++} -doped) by means of atomic layer deposition. The substrate is subsequently degreased three times with acetone in an ultrasound bath at
 35 room temperature and then cleaned in an oxygen plasma (< 0.3 mbar of O_2 , 2 min, 100 W). A 5 mM solution of the compound di-tert-butyl (3-(2,3-

5 difluoro-4-(4-pentylcyclohexyl)phenoxy)propyl)phosphonate (Synthesis Example 1) in decalin is applied to the substrate prepared in this way by spin coating at 4000 rpm for 30 s. The substrate is subsequently annealed at 110°C for 1 h, washed with isopropanol and dried under nitrogen.

The contact angle of water on the substrate is determined after each of the following steps:

Wafer (substrate) before treatment: 81°

10 Substrate after degreasing: 72°

After plasma treatment: 5°

After spin coating: 81°

After drying: 106°.

15 The value of 106° measured after completion of the production process indicates the presence of a stable monolayer.

The component is characterised electrically as described in WO2018/007337 A1 on pages 72 to 75 and exhibits memristive switching
20 behaviour.

Example 2: Production of an SAM on a TiN_x substrate

25 An approximately 30 nm thick titanium nitride layer is deposited on a silicon wafer (8 x 8 mm, p⁺⁺-doped) by sputtering. The other process steps are identical to those in Example 1.

The contact angle of water on the substrate is determined after each of the following steps:

30 Wafer (substrate) before treatment: 90°

Substrate after degreasing: 73°

After plasma treatment: 7°

After spin coating: 71°

35 After drying: 102°.

The value of 102° measured after completion of the production process indicates the presence of a stable monolayer.

Example 3: Production of a SAM on a glass substrate

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A glass substrate (8 x 8 mm) is degreased three times with isopropanol in an ultrasound bath at room temperature and then cleaned for 10 min with a freshly prepared mixture of conc. sulfuric acid and 30 per cent hydrogen peroxide (3:1, "piranha solution"), washed with water and dried under nitrogen. A 0.1 mM solution of the compound di-tert-butyl (3-(2,3-difluoro-4-(4-pentylcyclohexyl)phenoxy)propyl)phosphonate (Synthesis Example 1) in decalin is applied to the substrate prepared in this way by spin coating at 4000 rpm for 30 s. The substrate is subsequently annealed at 110°C for 1 h, washed with tetrahydrofuran and dried under nitrogen.

15

The contact angle of water on the substrate is determined after each of the following steps:

20

Glass substrate before treatment: 35°

Substrate after degreasing: 15°

After piranha treatment: 7°

After spin coating: 25°

25

After drying: 63° .

The value of 63° measured after completion of the production process indicates the presence of a stable monolayer.

30

Example 4: A 1-2 nm thick aluminium oxide layer is produced on a silicon wafer (8 x 8 mm, p^{++} -doped) by means of atomic layer deposition. The substrate is subsequently degreased three times with acetone in an ultrasound bath at room temperature and then cleaned in an oxygen plasma (< 0.3 mbar of O_2 , 1 min, 200 W). A 1 mM solution of the compound di-tert-butyl (11-(2,3-difluoro-4-(4-pentylcyclohexyl)phenoxy)undecyl)phosphonate in tetrahydrofuran is applied to the substrate prepared in this way by spin

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coating (application of 4 ml of solution over the course of 10 s with rotation at 150 rpm, subsequently at 3000 rpm for 35 s). The substrate is subsequently annealed at 160°C for 1 h, washed with 10 ml of tetrahydrofuran and dried under nitrogen. The component is characterised electrically with a mercury electrode as counterelectrode as described in WO2018/007337 A1 on pages 72 to 75 and exhibits memristive switching behaviour. The current/voltage curve is shown in Fig. 1. The so-called “memory window” (MW, Fig. 1, 1) is defined as the ratio of current in the low resistance state (I_{LRS}) to the current in the high resistance state (I_{HRS}) at half the maximum voltage, $MW = I_{LRS} / I_{HRS}$ at $\frac{1}{2} U_{max}$ and in the case of Example 4 is $MW = 9.6 \cdot 10^2$.

Comparative Example 1

A substrate, produced as in Example 4, is derivatised with the free phosphonic acid corresponding to the ester from Example 4 (11-(2,3-difluoro-4-(4-pentylcyclohexyl)phenoxy)undecyl)phosphonic acid, substance example 19 from WO2018/007337 A2) by dip coating. To this end, the substrate is dipped into a 1 mM solution of this phosphonic acid in tetrahydrofuran for 72 h, subsequently dried in a stream of nitrogen, dried at 120°C under nitrogen for 1 h, rinsed with 10 ml of tetrahydrofuran and dried again in a stream of nitrogen. The component is characterised electrically in the same way as the component from Example 4. The current/voltage curve is shown in Fig. 2. The memory window 1 is $MW = 1.3 \cdot 10^3$.

It can be seen that, surprisingly, the process according to the invention gives components which, within error tolerance, have the same “memory window” of $MW = \text{approx. } 1000$ as the components produced by the dip coating process known from the prior art.

Patent Claims

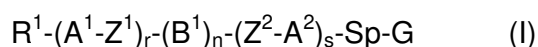
1. Process for the production of a component, comprising the following steps:

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- (1) provision of a substrate having a substrate surface,
(2) application of a solution comprising one or more compounds of the formula I to the substrate surface,
10 (3) heating of the substrate to a temperature in the range from 60°C to 300°C,

where formula I is defined as follows:

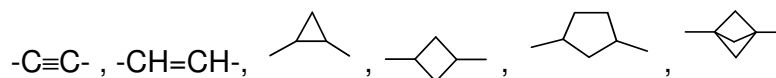
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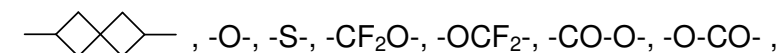
in which

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R^1 denotes H, an alkyl or alkoxy radical having 1 to 15 C atoms, where, in addition, one or more CH_2 groups in these radicals may each be replaced, independently of one another, by



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$-SiR^0R^{00}-$, $-NH-$, $-NR^0-$ or $-SO_2-$ in such a way that O atoms are not linked directly to one another, and in which, in addition, one or more H atoms may be replaced by halogen, CN, SCN or SF_5 ,

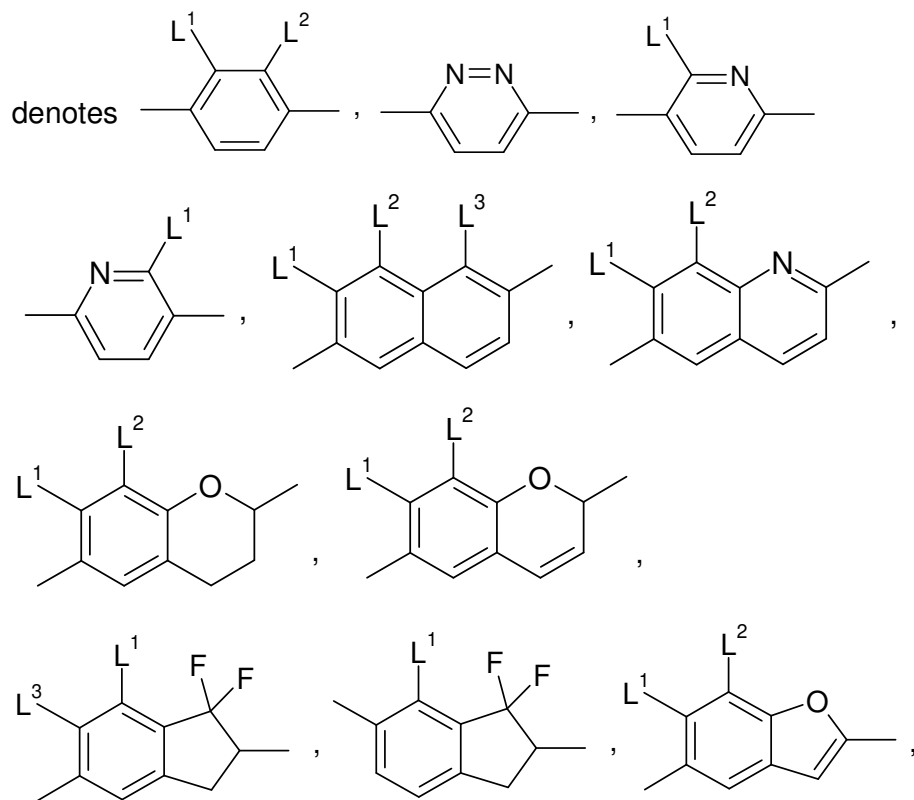
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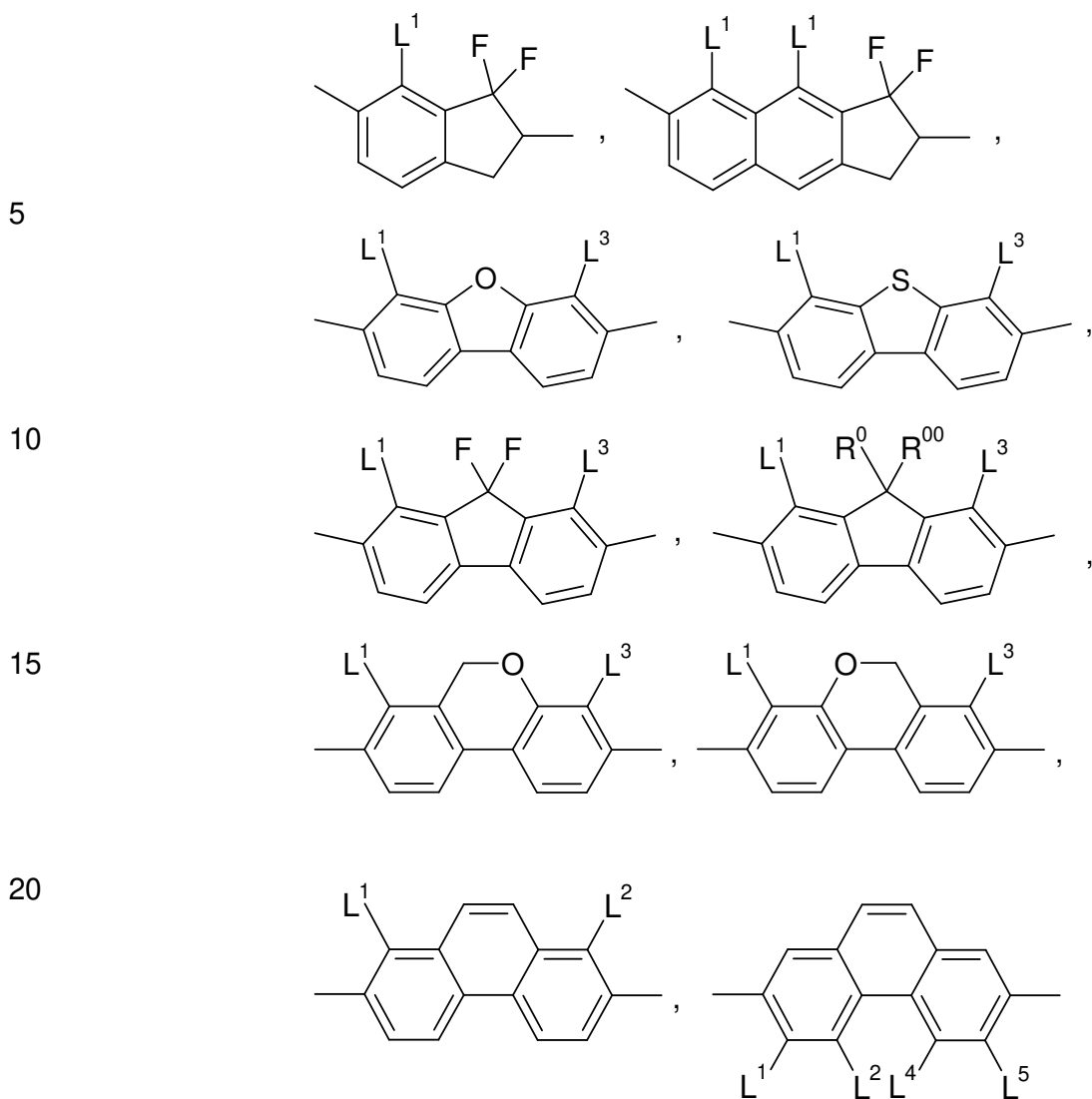
R^0 , R^{00} denote, identically or differently, an alkyl or alkoxy radical having 1 to 15 C atoms, in which, in addition, one or more H atoms may be replaced by halogen,

A¹, A² on each occurrence, identically or differently, denote an aromatic, heteroaromatic, alicyclic or heteroaliphatic ring having 4 to 25 ring atoms, which may also contain condensed rings and which may be mono- or polysubstituted by Y,

Y on each occurrence, identically or differently, denotes F, Cl, CN, SCN, SF₅ or straight-chain or branched, in each case optionally fluorinated, alkyl, alkoxy, alkylcarbonyl, alkoxy-carbonyl, alkylcarbonyloxy or alkoxy-carbonyloxy having 1 to 12 C atoms,

B¹





where the groups may be oriented in both directions,

30 L^1 to L^5 denote, independently of one another, F, Cl, Br, I, CN, SF_5 , CF_3 or OCF_3 , preferably Cl or F, where L^3 alternatively may also denote H,

35 Z^1, Z^2 on each occurrence, identically or differently, denote a single bond, $-CF_2O-$, $-OCF_2-$, $-CF_2S-$, $-SCF_2-$, $-CH_2O-$, $-OCH_2-$, $-C(O)O-$, $-OC(O)-$, $-C(O)S-$, $-SC(O)-$, $-CH_2-$, $-(CH_2)_2-$, $-(CH_2)_3-$, $-(CH_2)_4-$, $-CF_2-$, $-CF_2CF_2-$, $-CF_2CH_2-$, $-CH_2CF_2-$, $-CH=CH-$,

-CF=CF-, -CF=CH-, -CH=CF-, -(CH₂)₃O-, -O(CH₂)₃-, -C≡C-,
-O-, -S-, -C=N-, -N=C-, -N=N-, -N=N(O)-, -N(O)=N- or -N=C-
C=N-,

5

Sp denotes a spacer group or a single bond,

G denotes -SO₂OR^V, -OP(O)(OR^V)₂, -PO(OR^V)₂,
-C(OH)(PO(OR^V)₂)₂, -COOR^V or -Si(OR^V)₃,

10

R^V denotes secondary or tertiary alkyl having 3 to 20 C atoms,

r and s, independently of one another, denote 0, 1, 2 or 3,

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where $r + s \leq 4$, and

n denotes 0 or 1.

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2. Process according to Claim 1, where the substrate consists of a material selected from glass, metal oxide, metal nitride, metal oxy-nitride, element semiconductors, group III-V compound semiconductors, group II-VI compound semiconductors, metals, and conductive, oxidic materials.

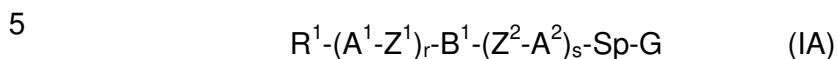
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3. Process according to Claim 1 or 2, where the substrate consists of a material selected from the element semiconductors Si, Ge, C, Sn, and Se, the compound semiconductors GaAs, InAs, InP, GaSb, TaN, TiN, MoN, WN and GaN, CdSe and ZnS, the metals Au, Ag, Cu, Al, W, Ta, Ti, Co, Mo, Pt, Ru and Mg, the conductive oxidic materials ITO, IGO, IGZO, AZO and FTO, or glass, SiO₂, Al₂O₃, TiO₂, HfO₂, ZrO₂, Si₃N₄, TaN_x, TiN_x, TiN_xO_y or TaN_xO_y.

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4. Process according to one or more of Claims 1 to 3, where the substrate surface has a coating consisting of a different material from the substrate.
- 5 5. Process according to Claim 4, where the coating of the substrate surface consists of an oxide and/or nitride of one or more metals or semi-metals.
- 10 6. Process according to one or more of Claims 1 to 5, where the solvent is removed by means of a stream of inert gas after application of the solution to a substrate.
- 15 7. Process according to one or more of Claims 1 to 6, where at least one of the steps is carried out at a pressure below 1000 hPa.
- 20 8. Process according to one or more of Claims 1 to 7, where the application of the solution to a substrate is carried out by spin coating.
- 25 9. Process for the production of a component, characterised in that the production is carried out by deposition of one or more compounds of the formula I according to Claim 1 from the gas phase.
- 30 10. Process according to Claim 9, where the deposition is carried out at a pressure of less than 500 hPa.
- 35 11. Process according to one or more of Claims 1 to 10, where n in formula I, as defined in Claim 1, denotes 1.
12. Component for use in an electronic element containing a self-assembled monolayer, formed and set up for the adoption of two switching states, where the component has been produced by the process according to one or more of Claims 1 to 11, with the proviso

that the self-assembled monolayer has been produced using one or more compounds of the formula IA, where formula IA is defined as follows:



where the groups and parameters occurring have the meanings indicated in Claim 1.

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13. Component according to Claim 12, where the one or more compounds of the formula IA are selected from the compounds of the formulae

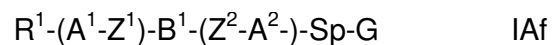
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in which R^1 , A^1 , A^2 , B^1 , Z^1 , Z^2 , Sp and G have the meanings indicated in Claim 1.

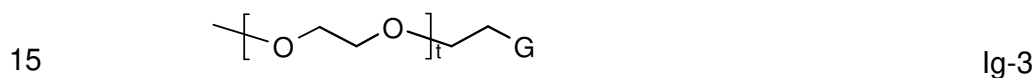
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14. Component according to Claim 12 or 13, where the material for the production of the self-assembled monolayer comprises one or more compounds of the formula Ig



in which R^2 has the meaning indicated for R^1 in Claim 1 and
G has the meaning indicated in Claim 1.

- 5 15. Component according to Claim 14, where the one or more compounds of the formula Ig are selected from the compounds of the formulae Ig-1 to Ig-3



in which

20 G denotes $-\text{PO}(\text{OR}^V)_2$ or $-\text{SO}_2\text{OR}^V$,

R^V denotes secondary or tertiary alkyl having 3 to 20 C atoms,

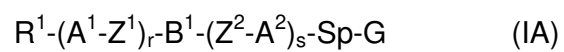
25 r denotes an integer from 1 to 20,

s denotes an integer from 1 to 18, and

30 t denotes an integer from 1 to 4.

16. Use of the component according to one or more of Claims 12 to 15 in a memristive electronic switching element.

- 35 17. Compound of the formula IA



in which the groups and parameters occurring have the meanings indicated in Claim 1.

5

18. Compound of the formula I according to Claim 17, in which

G denotes $-SO_2OR^V$ or $-PO(OR^V)_2$, and

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R^V denotes an isopropyl or tert-butyl radical.

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