Supporting Information

Experimental section

Tri-(*para*-tolyl)phosphinogold chloride

Tri(*para*-tolyl)phosphinogold chloride was synthesized according to a literature protocol.[S1]

1,1',1''-(Benzene-1,3,5-triyl)tris(*N*,*N*-dimethylmethanamine) (**17**)

1,1',1''-(Benzene-1,3,5-triyl)tris(*N*,*N*-dimethylmethanamine) (**17**) was synthesized according to a literature protocol.[S2]

Crystal Structure Determination:

Suitable crystals of the compounds **1, 2**, **3**, **10**, **11** and **12** were obtained by slow evaporation of saturated solutions of *n*-pentane (**10**, **11**), dichloromethane (**12**, **19**) and a 10:1 mixture of *n*-pentane/ dichloromethane (**1**, **2**, **3**). Compounds **4**, **5**, **6**, **7**, **8**, **9**, **15**, **20** and **21** were crystallized by cooling highly concentrated solutions of *n*-hexane to −40 °C. The single crystals were selected, coated with *paratone-N* oil, mounted on a glass fibre and transferred onto the goniometer of the diffractometer into a nitrogen-gas cold-stream solidifying the oil. Data collection were performed on a *SuperNova* diffractometer. Using Olex2 [S4] the structures were solved by direct methods and refined by full-matrix least-squares cycles (program SHELX-97).[S3] Crystal and refinement details, as well as CCDC numbers are provided in Tables S1-S4. CCDC 1512903-1512919 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.ac.uk/data_request/cif.

The structure of **1** reveals one heavy disordered pentane per unit cell, which couldn't be refined satisfactorily. This was included for sum formula and further calculations and was treated with the SQUEEZE procedure of Olex2.

Crystals of **8** were mixed crystals, 2,5% of the fluorine atoms are substituted with bromine. Crystals of **9** were merohedrically twinned with ratio 62:38. One of the crystallographic independent molecules is partly disordered (Si(4), F(8) to F(12) and C(21) to C(28)) with ratio 85:15. Crystal of **15** was pseudo-merohedrically twinned by a rotation of 180° around the c-axis (ratio 95:5), additionally it was mirror twinned (ratio 86:14). The SQUEEZE procedure of Olex2 was applied for the two isostructural compounds **18** and **19**, but the disordered solvent molecules could not be identified as one of the used solvents. So the sum formula and further calculations disregard this electron density. In **18** are both crystallographic independent molecules disordered around the three-fold axes with ratio of 85:15 and 66:34, respectively, in **19** only the second molecule (Si(2), F(2) and C(9) to C(32)) is disordered on two positions with a 66:34 distribution.

Table S1. Crystallographic data of **1**, **2**, **3** and **4**.

	1	**2**	**3**	**4**
formula	$C_{18}H_{12}FI_3Si$+ $C_{2.5}H_6$	$C_{18}H_{13}Br_3Si$	$C_{18}H_{12}Br_3FSi$	$C_{18}H_{12}BiFSi$
M_w	692.14	497.10	515.10	484.35
crystal size [mm]	0.19×0.04×0.03	0.12×0.11×0.07	0.21×0.16×0.02	0.38×0.20×0.04
temperature [K]	100.00(10)	99.98(16)	100.01(11)	99.9(3)
radiation	Cu Kα	Mo Kα	Mo Kα	Mo Kα
crystal system	trigonal	monoclinic	triclinic	orthorhombic
space group	$P3_1/c$	$P2_1/c$	$P\bar{1}$	$P2_12_12_1$
a [Å]	14.5289(4)	7.4821(4)	8.5263(1)	8.5601(2)
b [Å]	14.5289(4)	7.8061(4)	14.8043(2)	8.5931(2)
c [Å]	5.7867(2)	31.1863(14)	15.1065(2)	21.6023(5)
α [°]	90	90	105.90(1)	90
β [°]	90	92.95(1)	99.92(1)	90
γ [°]	120	90	95.79(1)	90
V [Å^3]	1057.85(6)	1819.05(15)	1784.24(5)	1589.01(6)
Z	2	4	4	4
$\rho_{calcd.}$ [mg mm^{-3}]	2.173	1.817	1.918	2.025
μ [mm^{-1}]	35.435	6.712	6.855	11.171
F(000)	646	960	992	904
2θ range [°]	7.0 to 144.9	5.4 to 60.0	3.4 to 60.2	5.1 to 60.0
Index ranges	−17 ≤ *h* ≤ 16 −17 ≤ *k* ≤ 17 −7 ≤ *l* ≤ 7	−10 ≤ *h* ≤ 10 −10 ≤ *k* ≤ 10 −43 ≤ *l* ≤ 43	−12 ≤ *h* ≤ 12 −20 ≤ *k* ≤ 20 −21 ≤ *l* ≤ 21	−11 ≤ *h* ≤ 11 −12 ≤ *k* ≤ 12 −30 ≤ *l* ≤ 30
total reflns	17665	19343	85951	57635
unique reflns	1379	5267	10469	4589
R_{int}	0.0712	0.0351	0.0501	0.0599
reflns [$I>2\sigma(I)$]	1350	4427	8916	4447
parameters	70	203	415	190
R_1/ wR_2 [$I>2\sigma(I)$]	0.0288/0.0781	0.0279/0.0517	0.0268/0.0591	0.0229/0.0516
R_1/ wR_2 (all data)	0.0296/0.0792	0.0396/0.0553	0.0364/0.0626	0.0248/0.0528
$\rho_{max/min}$ [*e* Å^{-3}]	0.45−1.27	0.55/−0.70	0.99/−0.60	1.94/−1.91
Flack parameter	-0.018(9)			-0-033(3)
CCDC no.	1512903	1512904	1512905	1512906

Table S2. Crystallographic data of **5**, **6**, **7** and **8**.

	5	**6**	**7**	**8**
formula	$C_{24}H_{33}FSi_4$	$C_{24}H_{30}F_4Si_4$	$C_{24}H_{30}Cl_3FSi_4$	$C_{24}H_{30}Br_{3.03}F_{0.97}Si_4$
M_w	452.86	506.84	556.19	691.12
crystal size [mm]	0.68×0.42×0.14	0.51×0.25×0.03	0.19×0.10×0.01	0.17×0.15×0.07
temperature [K]	100.00(11)	100.00(10)	100.01(10)	100.01(10)
radiation	Mo Kα	Cu Kα	Cu Kα	Cu Kα
crystal system	monoclinic	monoclinic	triclinic	triclinic
space group	$P2_1/n$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a [Å]	18.3989(4)	18.1783(10)	8.8156(11)	10.2157(1)
b [Å]	13.8715(3)	9.5489(3)	9.6417(12)	11.1320(2)
c [Å]	21.2423(5)	30.1357(13)	17.3878(16)	13.9024(2)
α [°]	90	90	102.50(1)	98.42(1)
β [°]	105.04(1)	91.51(1)	91.62(1)	103.53(1)
γ [°]	90	90	97.13(1)	104.87(1)
V [Å^3]	5235.9(2)	5229.2(4)	1429.4(3)	1449.33(3)
Z	8	8	2	2
$\rho_{calcd.}$ [mg mm^{-3}]	1.149	1.228	1.289	1.584
μ [mm^{-1}]	0.243	2.455	4.656	6.933
F(000)	1936	2128	580	689
2θ range [°]	3.4 to 54.0	5.9 to 134.0	5.2 to 144.0	6.7 to 143.9
Index ranges	$-23 \le h \le 23$ $-17 \le k \le 17$ $-27 \le l \le 26$	$-21 \le h \le 21$ $-11 \le k \le 11$ $-35 \le l \le 35$	$-10 \le h \le 10$ $-11 \le k \le 11$ $-21 \le l \le 21$	$-12 \le h \le 12$ $-13 \le k \le 13$ $-17 \le l \le 17$
total reflns	155423	93632	25090	83630
unique reflns	11387	9331	5612	5695
R_{int}	0.0411	0.0704	0.0404	0.0278
reflns [$I>2\sigma(I)$]	10247	8885	4877	5571
parameters	568	590	311	415
R_1/ wR_2 [$I>2\sigma(I)$]	0.0322/0.0986	0.0851/0.2280	0.0365/0.0948	0.0244/0.0629
R_1/ wR_2 (all data)	0.0406/0.1125	0.0879/0.2305	0.0434/0.1001	0.0249/0.0632
$\rho_{max/min}$ [*e* Å^{-3}]	0.53/−0.73	1.35/−0.50	1.72/−0.36	0.78/−0.60
CCDC no.	1512907	1512908	1512909	1512910

Table S3. Crystallographic data of **9**, **10**, **11** and **12**.

	9	**10**	**11**	**12**
formula	$C_{42}H_{30}F_{16}Si_4$	$C_{33}H_{40}Si_4$	$C_{33}H_{39}FSi_4$	$C_{24}H_{15}FSi$
M_w	951.02	549.01	567.00	350.45
crystal size [mm]	0.21×0.14×0.14	0.27×0.16×0.09	0.19×0.11×0.02	0.16×0.07×0.02
temperature [K]	100.01(10)	100.01(10)	99.98(1)	100.00(10)
radiation	Cu Kα	Cu Kα	Cu Kα	Cu Kα
crystal system	trigonal	triclinic	triclinic	monoclinic
space group	$R\bar{3}$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a [Å]	20.8142(1)	10.5748(1)	10.7140(4)	9.3691(3)
b [Å]	20.8142(1)	10.9915(2)	12.9359(4)	15.3606(6)
c [Å]	32.6414(1)	16.0380(2)	13.8460(4)	12.4364(4)
α [°]	90	83.10(1)	71.09(1)	90
β [°]	90	82.01(1)	85.43(1)	92.00(1)
γ [°]	120	66.91(1)	67.61(1)	90
V [Å^3]	12246.66(12)	1693.71(4)	1676.37(11)	1788.70(10)
Z	12	2	2	4
$\rho_{calcd.}$ [mg mm^{-3}]	1.547	1.077	1.123	1.301
μ [mm^{-1}]	2.317	1.756	1.834	1.260
F(000)	5784	588	604	728
2θ range [°]	5.6 to 143.8	5.6 to 144.0	6.8 to 144.2	9.2 to 150.3
Index ranges	−25 ≤ *h* ≤ 25 −25 ≤ *k* ≤ 25 −40 ≤ *l* ≤ 40	−11 ≤ *h* ≤ 13 −13 ≤ *k* ≤ 13 −19 ≤ *l* ≤ 19	−11 ≤ *h* ≤ 13 −15 ≤ *k* ≤ 15 −17 ≤ *l* ≤ 16	−11 ≤ *h* ≤ 9 −18 ≤ *k* ≤ 19 −15 ≤ *l* ≤ 11
total reflns	147651	61286	27635	12556
unique reflns	5344	6651	6581	3631
R_{int}	0.0298	0.0233	0.0332	0.0581
reflns [*I*>2σ(*I*)]	5318	6491	5699	2780
parameters	399	347	352	295
R_1/ wR_2 [*I*>2σ(*I*)]	0.0355/0.1010	0.0359/0.0962	0.0325/0.0820	0.0444/0.0995
R_1/ wR_2 (all data)	0.0356/0.1011	0.0365/0.0966	0.0400/0.0871	0.0660/0.1109
$\rho_{max/min}$ [*e* Å^{-3}]	0.52/−0.24	0.32/−0.32	0.35/−0.27	0.34/−0.36
CCDC no.	1512911	1512912	1512913	1512914

Table S4. Crystallographic data of **15**, **18**, **19**, **20** and **21**.

	15	**18**	**19**	**20**	**21**
formula	$C_{33}H_{39}FSiSn_3$	$C_{24}H_{21.96}Si$	$C_{24}H_{21}FSi$	$C_{27}H_{33}Cl_6FSi_4$	$C_{27}H_{33}F_7Si_4$
M_w	838.80	338.47	356.50	701.59	602.89
crystal size [mm]	0.12×0.06×0.02	0.04×0.02×0.02	0.15×0.11×0.07	0.19×0.14×0.13	0.16×0.10×0.04
temperature [K]	100.00(10)	100.01(10)	100.0(3)	100.0(1)	99.96(12)
radiation	Cu Kα	Cu Kα	Cu Kα	Cu Kα	Cu Kα
crystal system	monoclinic	trigonal	trigonal	monoclinic	monoclinic
space group	$P2_1$	$R\bar{3}$	$R\bar{3}$	$P2_1/c$	$P2_1/c$
a [Å]	12.8067(1)	23.2744(11)	23.2278(6)	18.6245(1)	18.6337(4)
b [Å]	41.3809(2)	23.2744(11)	23.2278(6)	16.0957(1)	9.3913(2)
c [Å]	13.1707(1)	25.4899(7)	25.4534(7)	11.4259(1)	17.3787(3)
α [°]	90	90	90	90	90
β [°]	90.21(1)	90	90	98.23(1)	98.13(1)
γ [°]	90	120	120	90	90
V [Å^3]	6979.77(9)	11958.0(11)	11893.0(7)	3389.93(3)	3010.62(10)
Z	8	24	24	4	4
$\rho_{calcd.}$ [mg mm^{-3}]	1.596	1.128	1.195	1.375	1.330
μ [mm^{-1}]	17.452	1.032	1.138	6.167	2.367
F(000)	3280	4319	4512	1448	1256
2θ range [°]	6.4 to 144.7	5.6 to 154.2	5.6 to 145.7	7.3 to 153.1	9.6 to 144.2
Index ranges	$-15 \le h \le 15$ $-51 \le k \le 50$ $-16 \le l \le 15$	$-29 \le h \le 28$ $-29 \le k \le 29$ $-32 \le l \le 32$	$-28 \le h \le 28$ $-28 \le k \le 28$ $-31 \le l \le 29$	$-23 \le h \le 23$ $-20 \le k \le 19$ $-14 \le l \le 14$	$-23 \le h \le 21$ $-5 \le k \le 11$ $-20 \le l \le 21$
total reflns	243961	74800	70643	121594	14149
unique reflns	27491	5236	5207	7099	5932
R_{int}	0.0639	0.0765	0.0785	0.0285	0.0314
reflns [$I>2\sigma(I)$]	26648	3844	4490	6962	5008
parameters	1408	491	476	366	346
R_1/ wR_2 [$I>2\sigma(I)$]	0.0376/0.0937	0.0625/0.1732	0.0466/0.01207	0.0249/0.0650	0.0500/0.1317
R_1/ wR_2 (all data)	0.0394/0.0955	0.0813/0.1852	0.0527/0.1248	0.0253/0.0654	0.0586/0.1389
$\rho_{max/min}$ [eÅ^{-3}]	0.85/−1.64	0.19/−0.30	0.41/−0.27	0.49/−0.53	0.98/−0.54
CCDC no.	1512915	1512916	1512917	1512918	1512919

Crystal structure of tris(2-iodophenyl)fluorosilane (1)

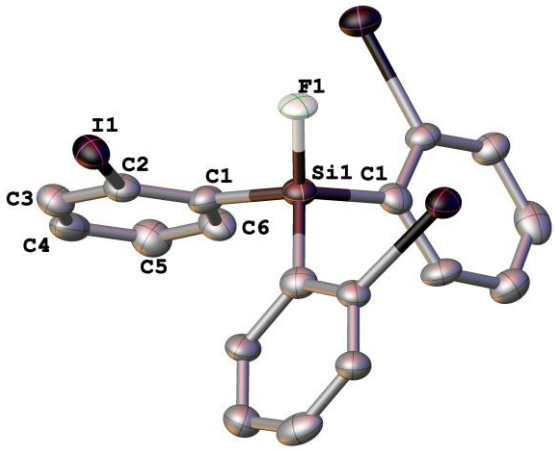

Figure S1 Molecular structure of tris(2-iodophenyl)fluorosilane (**1**). Displacement ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity. The electron density of one highly disordered pentane per unit cell was masked using OLEX2 (details: _smtbx_masks_special_details). The solvent was left in the formula sum for further calculations. Selected bond lengths [Å] and angles [deg]: C(1)–C(2) 1.415(11), C(2)–C(3) 1.378(11), C(3)–C(4) 1.364(15), C(4)–C(5) 1.401(14), C(5)–C(6) 1.392(12), C(1)–C(6) 1.394(11), C(1)–Si(1) 1.874(8), Si(1)–F(1) 1.592(8), C(2)–I(1) 2.120(7); C(1)–C(2)–C(3) 122.2(7), C(2)–C(3)–C(4) 119.8(8), C(3)–C(4)–C(5) 120.9(8), C(4)–C(5)–C(6) 118.2(9), C(5)–C(6)–C(1) 122.9(8), C(1)–Si(1)–F(1) 110.6(3), C(1)–Si(1)–C(1) 108.3(3), C(1)–C(2)–I(1) 121.6(6).

Crystal structure of tris(2-bromophenyl)silane (2)

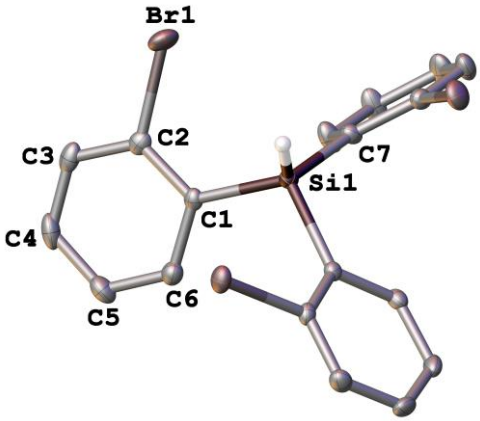

Figure S2 Molecular structure of tris(2-bromophenyl)silane (**2**). Displacement ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond length [Å] and angles [deg]: C(1)–C(2) 1.400(3), C(2)–C(3) 1.387(3), C(3)–C(4) 1.379(3), C(4)–C(5) 1.398(3), C(5)–C(6) 1.383(3), C(1)–C(6) 1.407(3), C(1)–Si(1) 1.881(2), C(2)–Br(1) 1.914(2); C(1)–C(2)–C(3) 123.3(2), C(2)–C(3)–C(4) 119.4(2), C(3)–C(4)–C(5) 119.5(2), C(4)–C(5)–C(6) 120.1(2), C(1)–Si(1)–C(7) 108.8(1), C(1)–C(2)–Br(1) 118.8(2).

Crystal structure of tris(2-bromophenyl)fluorosilane (3)

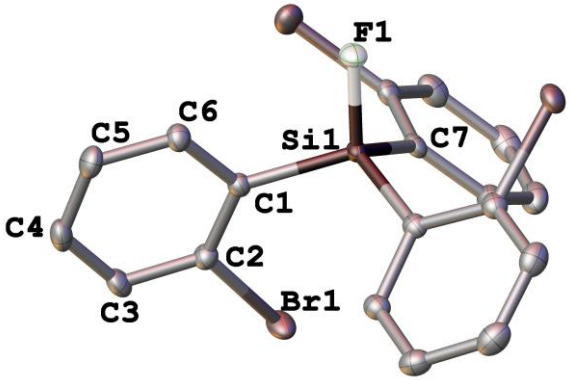

Figure S3 Molecular structure of tris(2-bromophenyl)fluorosilane (**3**). Displacement ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [deg]: C(1)–C(2) 1.396(3), C(2)–C(3) 1.388(3), C(3)–C(4) 1.389(3), C(4)–C(5) 1.388(3), C(5)–C(6) 1.386(3), C(1)–C(6) 1.411(3), C(1)–Si(1) 1.865(2), Si(1)–F(1) 1.604(1), C(2)–Br(1) 1.909(2); C(1)–C(2)–C(3) 123.0(2), C(2)–C(3)–C(4) 119.1(2), C(3)–C(4)–C(5) 120.0(2), C(4)–C(5)–C(6) 120.1(2), C(5)–C(6)–C(1) 121.7(2), C(1)–Si(1)–F(1) 103.9(1), C(1)–Si(1)–C(7) 115.7(1), C(1)–C(2)–Br(1) 120.1(2).

Crystal structure of 9-bisma-10-fluorosilyltriptycene (4)

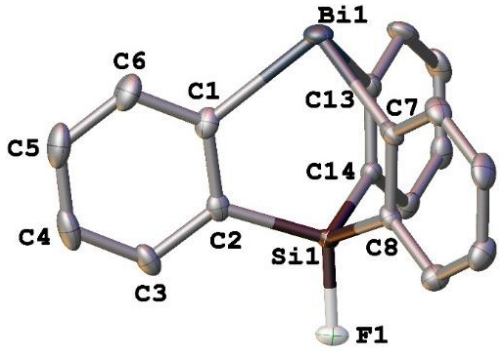

Figure S4 Molecular structure of 9-bisma-10-fluorosilyltriptycene (**4**). Displacement ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [deg]: C(1)–C(2) 1.406(7), C(2)–C(3) 1.405(7), C(3)–C(4) 1.390(8), C(4)–C(5) 1.389(10), C(5)–C(6) 1.384(9), C(1)–C(6) 1.392(7), C(1)–Bi(1) 2.271(5), C(2)–Si(1) 1.847(5), Si(1)–F(1) 1.598(3); C(1)–C(2)–C(3) 118.6(5), C(2)–C(3)–C(4) 120.2(5), C(3)–C(4)–C(5) 120.3(5), C(4)–C(5)–C(6) 120.4(6), C(1)–C(6)–C(5) 119.8(6), C(6)–C(1)–Bi(1) 119.1(4), C(1)–Bi(1)–C(7) 89.6(2), C(3)–C(2)–Si(1) 125.7(4), C(2)–Si(1)–C(8) 108.0(2), C(2)–Si(1)–F(1) 110.8(2), Bi(1)–C(1)–C(2) 120.1(4), C(1)–C(2)–Si(1) 115.6(4).

Crystal structure of tris(2-(dimethylsilyl)phenyl)fluorosilane (5)

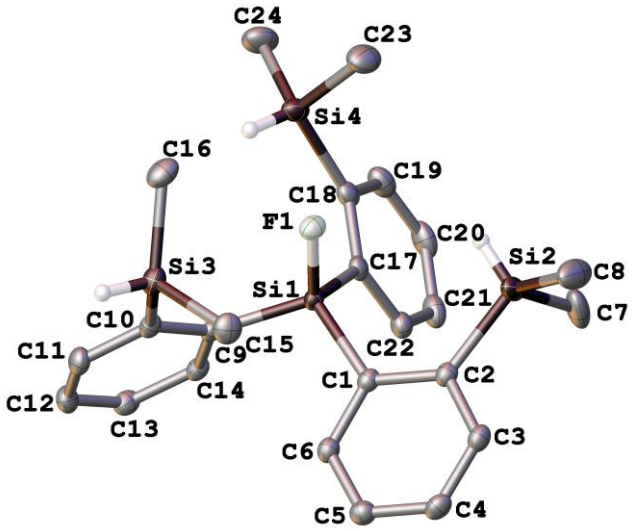

Figure S5 Molecular structure of tris(2-(dimethylsilyl)phenyl)fluorosilane (**5**). Displacement ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [deg]: C(1)–C(2) 1.425(2), C(2)–C(3) 1.402(2), C(3)–C(4) 1.389(2), C(4)–C(5) 1.379(2), C(5)–C(6) 1.392(2), C(1)–C(6) 1.400(2), C(1)–Si(1) 1.877(2), Si(1)–F(1) 1.602(1), C(2)–Si(2) 1.882(2), Si(2)–C(7) 1.864(2); C(1)–C(2)–C(3) 118.1(1), C(2)–C(3)–C(4) 122.2(1), C(3)–C(4)–C(5) 119.6(1), C(4)–C(5)–C(6) 119.5(1), C(5)–C(6)–C(1) 122.1(1), C(1)–Si(1)–F(1) 107.4(1), C(1)–C(2)–Si(2) 125.5(1), C(1)–Si(1)–C(9) 108.8(1), C(2)–Si(2)–C(7) 109.8(1), C(7)–Si(2)–C(8) 108.4(1).

Crystal structure of tris(2-(fluorodimethylsilyl)phenyl)fluorosilane (6)

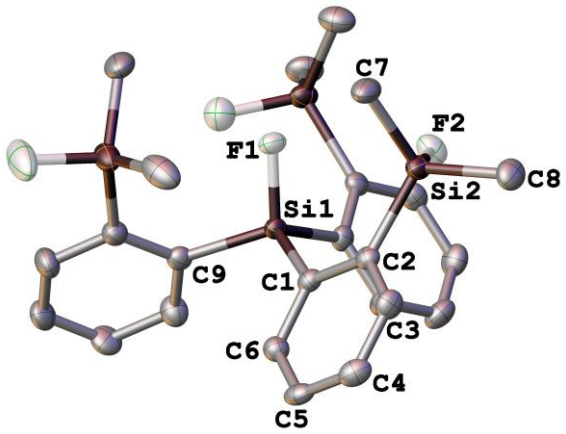

Figure S6 Molecular structure of tris(2-(fluorodimethylsilyl)phenyl)fluorosilane (**6**). Displacement ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [deg]:C(1)–C(2) 1.413(7), C(2)–C(3) 1.387(7), C(3)–C(4) 1.405(8), C(4)–C(5) 1.364(8), C(5)–C(6) 1.387(7), C(1)–C(6) 1.402(7), C(1)–Si(1) 1.877(5), Si(1)–F(1) 1.608(3), C(2)–Si(2) 1.884(5), Si(2)–C(7) 1.845(6), Si(2)–F(2) 1.601(3); C(1)–C(2)–C(3) 118.5(4), C(2)–C(3)–C(4) 121.9(5), C(3)–C(4)–C(5) 119.2(5), C(4)–C(5)–C(6) 120.2(5), C(5)–C(6)–C(1) 121.4(5), C(1)–Si(1)–F(1) 106.2(2), C(1)–Si(1)–C(9) 110.4(2), C(1)–C(2)–Si(2) 126.3(4), C(2)–Si(2)–C(7) 113.1(2), C(7)–Si(2)–C(8) 110.3(3), C(7)–Si(2)–F(2) 108.7(3).

Crystal structure of tris(2-(chlorodimethylsilyl)phenyl)fluorosilane (7)

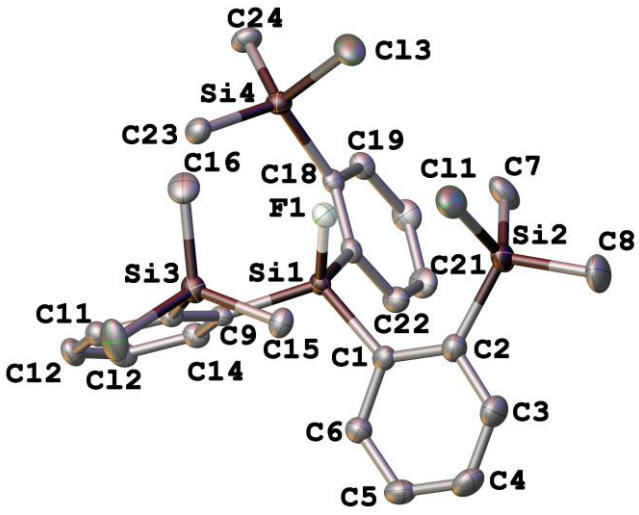

Figure S7 Molecular structure of tris(2-(chlorodimethylsilyl)phenyl)fluorosilane (**7**). Displacement ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [deg]: C(1)–C(2) 1.420(3), C(2)–C(3) 1.402(3), C(3)–C(4) 1.389(4), C(4)–C(5) 1.380(4), C(5)–C(6) 1.390(3), C(1)–C(6) 1.398(3), C(1)–Si(1) 1.876(2), Si(1)–F(1) 1.607(1), C(2)–Si(2) 1.889(2), Si(2)–C(7) 1.848(3), Si(2)–Cl(1) 2.081(1); C(1)–C(2)–C(3) 117.6(2), C(2)–C(3)–C(4) 122.6(2), C(3)–C(4)–C(5) 119.5(2), C(4)–C(5)–C(6) 119.2(2), C(5)–C(6)–C(1) 122.3(2), C(1)–Si(1)–F(1) 108.5(1), C(1)–Si(1)–C(9) 111.9(1), C(1)–C(2)–Si(2) 127.1(2), C(2)–Si(2)–C(7) 114.5(1), C(7)–Si(2)–C(8) 109.9(1), C(7)–Si(2)–Cl(1) 107.0(1).

Crystal structure of tris(2-(bromodimethylsilyl)phenyl)fluorosilane (8)

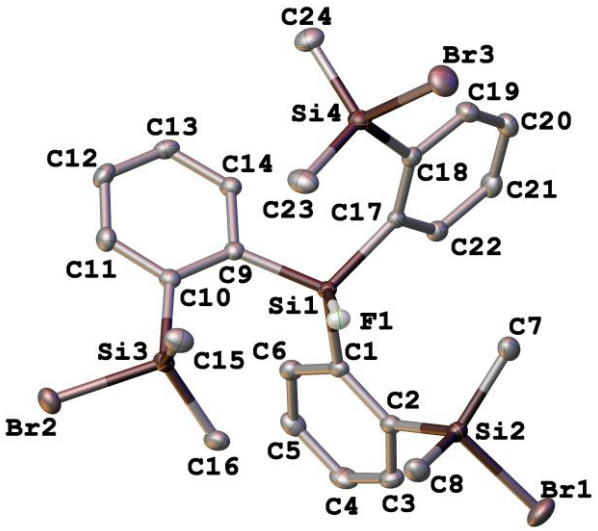

Figure S8 Molecular structure of tris(2-(bromodimethylsilyl)phenyl)fluorosilane (**8**). Displacement ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity. Mixed crystal of two compounds 0.975($C_{24}H_{30}Br_3FSi_4$), 0.025($C_{24}H_{30}Br_4Si_4$). Selected bond lengths [Å] and angles [deg]: C(1)–C(2) 1.426(3), C(2)–C(3) 1.404(3), C(3)–C(4) 1.388(3), C(4)–C(5) 1.378(3), C(5)–C(6) 1.392(3), C(1)–C(6) 1.397(3), C(1)–Si(1) 1.874(2), Si(1)–F(1) 1.597(2), C(2)–Si(2) 1.897(2), Si(2)–C(7) 1.856(2), Si(2)–Br(1) 2.257(1); C(1)–C(2)–C(3) 117.5(2), C(2)–C(3)–C(4) 122.3(2), C(3)–C(4)–C(5) 120.1(2), C(4)–C(5)–C(6) 119.1(2), C(5)–C(6)–C(1) 122.2(2), C(1)–Si(1)–F(1) 106.5(1), C(1)–Si(1)–C(9) 111.5(1), C(1)–C(2)–Si(2) 124.2(1), C(2)–Si(2)–C(7) 114.1(1), C(7)–Si(2)–C(8) 112.5(1), C(7)–Si(2)–Br(1) 104.1(1).

Crystal structure of tris(2-(pentafluorophenyldimethylsilyl)phenyl)fluorosilane (9)

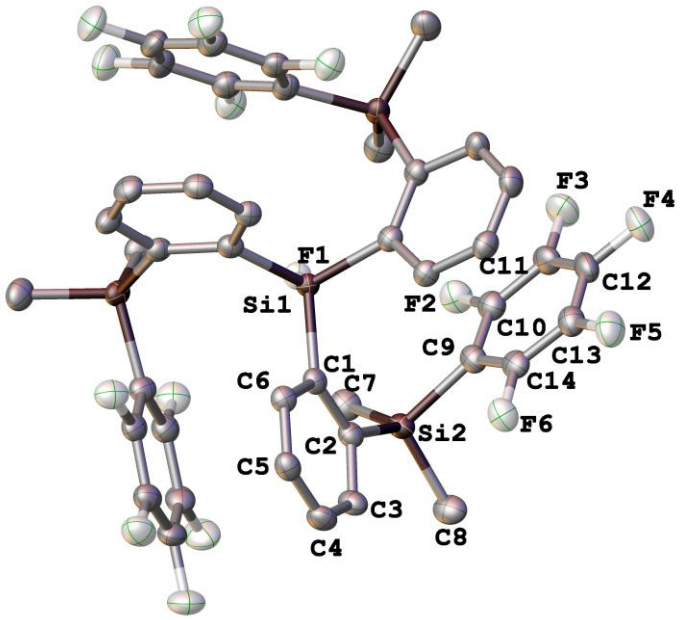

Figure 9 Molecular structure of tris(2-(pentafluorophenyldimethylsilyl)phenyl)fluorosilane (**9**). Displacement ellipsoids are drawn at 50% probability level. Hydrogen atoms and second molecule are omitted for clarity. Selected bond lengths [Å] and angles [deg]: C(1)–C(2) 1.428(3), C(2)–C(3) 1.418(3), C(3)–C(4) 1.378(3), C(4)–C(5) 1.375(4), C(5)–C(6) 1.394(3), C(1)–C(6) 1.404(3), C(1)–Si(1) 1.882(2), Si(1)–F(1) 1.598(2), C(2)–Si(2) 1.899(2), Si(2)–C(7) 1.857(3), Si(2)–C(9) 1.896(3), C(9)–C(10) 1.390(3), C(10)–C(11) 1.387(4), C(11)–C(12) 1.372(4), C(12)–C(13) 1.397(4), C(13)–C(14) 1.370(4), C(14)–C(9) 1.390(3), C(10)–F(2) 1.343(3); C(1)–C(2)–C(3) 117.6(2), C(2)–C(3)–C(4) 122.1(2), C(3)–C(4)–C(5) 120.6(2), C(4)–C(5)–C(6) 118.9(2), C(5)–C(6)–C(1) 122.5(2), C(1)–Si(1)–F(1) 109.4(1), C(1)–Si(1)–C(1) 109.5(1), C(1)–C(2)–Si(2) 128.4(2), C(2)–Si(2)–C(7) 113.9(1), C(2)–Si(2)–C(9) 108.0(1), Si(2)–C(9)–C(10) 126.0(2), C(9)–C(10)–C(11) 122.8(2), C(10)–C(11)–C(12) 119.6(2), C(11)–C(12)–C(13) 119.9(2), C(12)–C(13)–C(14) 118.3(2), C(13)–C(14)–C(9) 124.3(2).

Crystal structure of tris(2-((trimethylsilyl)ethynyl)phenyl)silane (10)

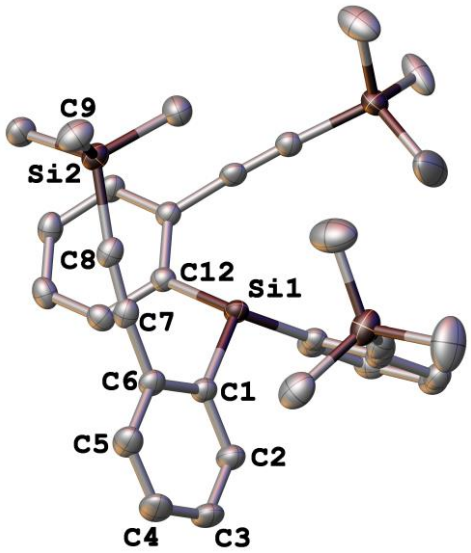

Figure S10 Molecular structure of tris(2-((trimethylsilyl)ethynyl)phenyl)silane (**10**). Displacement ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [deg]: C(1)–C(2) 1.395(2), C(2)–C(3) 1.388(2), C(3)–C(4) 1.382(3), C(4)–C(5) 1.384(2), C(5)–C(6) 1.400(2), C(1)–C(6) 1.413(2), C(1)–Si(1) 1.881(1), C(6)–C(7) 1.438(2), C(7)–C(8) 1.207(2), C(8)–Si(2) 1.844(2), Si(2)–C(9) 1.854(2); C(1)–C(2)–C(3) 121.4(2), C(2)–C(3)–C(4) 120.0(2), C(3)–C(4)–C(5) 120.3(2), C(4)–C(5)–C(6) 120.0(2), C(5)–C(6)–C(1) 120.3(1), C(1)–Si(1)–C(12) 108.5(1), C(1)–C(6)–C(7) 118.1(1), C(6)–C(7)–C(8) 172.8(2), C(7)–C(8)–Si(2) 173.4(1), C(8)–Si(2)–C(9) 107.8(1).

Crystal structure of tris(2-((trimethylsilyl)ethynyl)phenyl)fluorosilane (11)

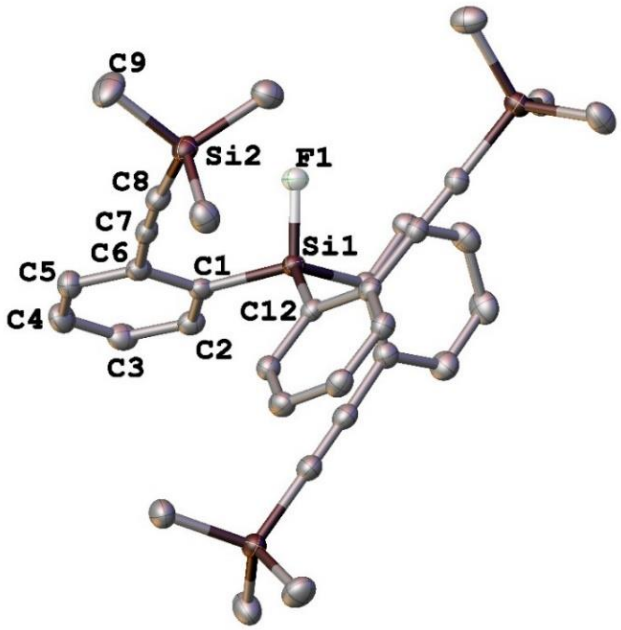

Figure S11 Molecular structure of tris(2-((trimethylsilyl)ethynyl)phenyl)fluorosilane (**11**). Displacement ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [deg]: C(1)–C(2) 1.394(2), C(2)–C(3) 1.393(2), C(3)–C(4) 1.385(2), C(4)–C(5) 1.382(2), C(5)–C(6) 1.401(2), C(1)–C(6) 1.415(2), C(1)–Si(1) 1.875(1), Si(1)–F(1) 1.600(1), C(6)–C(7) 1.437(2), C(7)–C(8) 1.205(2), C(8)–Si(2) 1.841(2), Si(2)–C(9) 1.858(2); C(1)–C(2)–C(3) 121.5(1), C(2)–C(3)–C(4) 119.8(1), C(3)–C(4)–C(5) 120.3(1), C(4)–C(5)–C(6) 120.2(2), C(5)–C(6)–C(1) 120.4(1), C(1)–Si(1)–C(12) 111.0(1), C(1)–C(6)–C(7) 119.5(1), C(6)–C(7)–C(8) 175.5(2), C(7)–C(8)–Si(2) 174.6(1), C(8)–Si(2)–C(9) 108.4(1).

Crystal structure of tris(2-ethynylphenyl)fluorosilane (12)

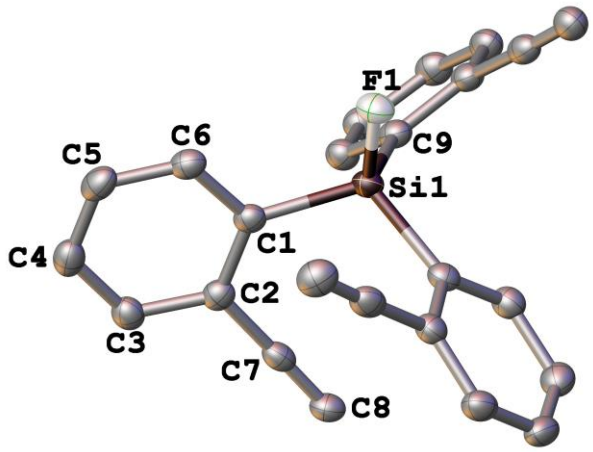

Figure S12 Molecular structure of tris(2-ethynylphenyl)fluorosilane (**12**). Displacement ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [deg]:C(1)–C(2) 1.415(3), C(2)–C(3) 1.405(3), C(3)–C(4) 1.378(3), C(4)–C(5) 1.386(4), C(5)–C(6) 1.387(3), C(1)–C(6) 1.398(3), C(1)–Si(1) 1.865(2), Si(1)–F(1) 1.599(1), C(2)–C(7) 1.447(3), C(7)–C(8) 1.161(3); C(1)–C(2)–C(3) 120.3(2), C(2)–C(3)–C(4) 120.3(2), C(3)–C(4)–C(5) 120.1(2), C(4)–C(5)–C(6) 120.1(2), C(5)–C(6)–C(1) 121.6(2), C(1)–Si(1)–F(1) 105.8(1), C(1)–Si(1)–C(9) 109.2(1), C(1)–C(2)–C(7) 120.8(2), C(2)–C(7)–C(8) 177.6(2).

Crystal structure of tris(2-((trimethylstannyl)ethynyl)phenyl)fluorosilane (15)

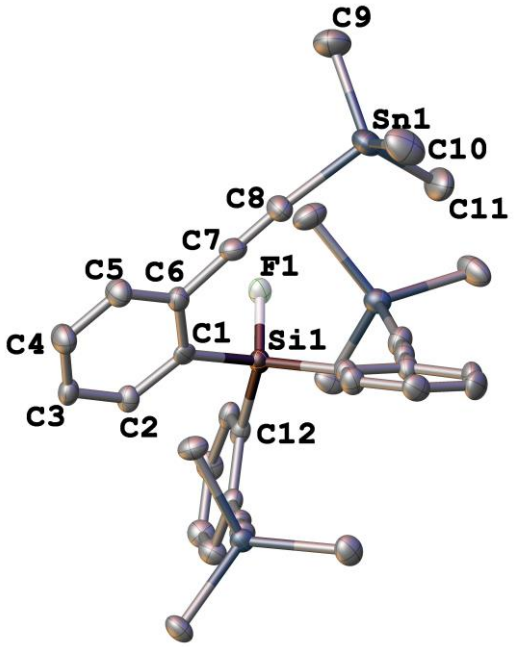

Figure S13 Molecular structure of tris(2-((trimethylstannyl)ethynyl)phenyl)fluorosilane (**15**). Displacement ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity. Refined as a 4-component twin. Selected bond lengths [Å] and angles [deg]: C(1)–C(2) 1.400(12), C(2)–C(3) 1.386(13), C(3)–C(4) 1.401(14), C(4)–C(5) 1.391(14), C(5)–C(6) 1.389(14), C(1)–C(6) 1.422(13), C(1)–Si(1) 1.872(10), Si(1)–F(1) 1.605(6), C(6)–C(7) 1.437(13), C(7)–C(8) 1.202(14), C(8)–Sn(1) 2.112(10), Sn(1)–C(9) 2.135(13); C(1)–C(2)–C(3) 122.0(9), C(2)–C(3)–C(4) 119.7(9), C(3)–C(4)–C(5) 119.3(10), C(4)–C(5)–C(6) 121.1(9), C(5)–C(6)–C(1) 120.2(8), C(6)–C(1)–Si(1) 122.6(7), C(1)–Si(1)–F(1) 106.4(3), C(1)–Si(1)–C(12) 114.9(4), C(6)–C(7)–C(8) 178.3(11), C(7)–C(8)–Sn(1) 174.4(9) C(8)–Sn(1)–C(9) 106.6(5).

Crystal structure of tris(2-vinylphenyl)silane (18)

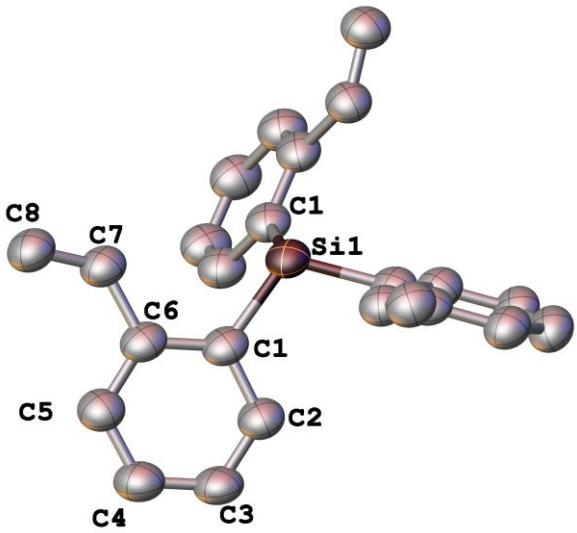

Figure S14 Molecular structure of tris(2-vinylphenyl)silane (**18**). Displacement ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity. Disorder of both molecules on two positions, the one on the trifold axis with a 85:15 distribution, the one on the general position with a 66:34 distribution. Hydrogens bonded to silicon were refined isotropically, except the one of Si(1b) which could not be located. Selected bond lengths [Å] and angles [deg]: C(1)–C(2) 1.398(4), C(2)–C(3) 1.380(6), C(3)–C(4) 1.371(6), C(4)–C(5) 1.397(5), C(5)–C(6) 1.398(5), C(1)–C(6) 1.412(5), C(1)–Si(1) 1.882(3), C(6)–C(7) 1.479(5), C(7)–C(8) 1.326(4); C(1)–C(2)–C(3) 121.5(3), C(2)–C(3)–C(4) 120.2(4), C(3)–C(4)–C(5) 120.1(4), C(4)–C(5)–C(6) 120.3(3), C(5)–C(6)–C(1) 119.6(4), C(6)–C(1)–Si(1) 123.3(3), (C2)–C(1)–Si(1) 118.4(2), C(1)–Si(1)–C(1) 109.7(1), C(1)–C(6)–C(7) 120.2(3), C(6)–C(7)–C(8) 126.3(3).

Crystal structure of tris(2-vinylphenyl)fluorosilane (19)

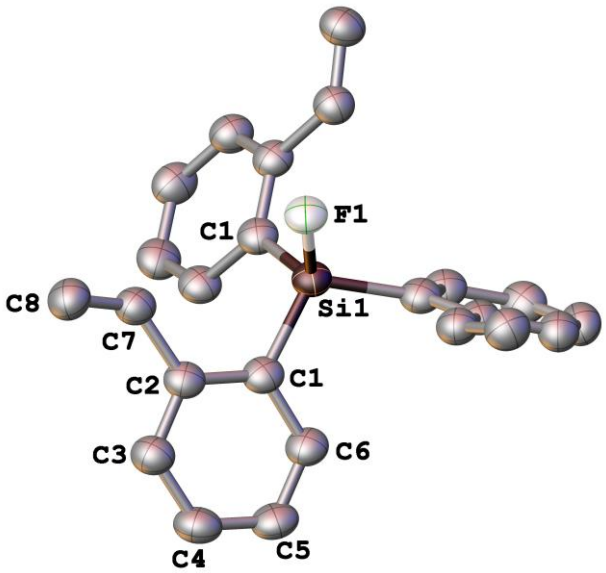

Figure S15 Molecular structure of tris(2-vinylphenyl)fluorosilane (**19**). Displacement ellipsoids are drawn at 50% probability level. Hydrogen atoms and second molecule are omitted for clarity. Selected bond lengths [Å] and angles [deg]: C(1)–C(2) 1.412(2), C(2)–C(3) 1.394(2), C(3)–C(4) 1.391(2), C(4)–C(5) 1.377(2), C(5)–C(6) 1.383(2), C(1)–C(6) 1.404(2), C(1)–Si(1) 1.866(2), Si(1)–F(1) 1.614(2), C(2)–C(7) 1.484(2), C(7)–C(8) 1.322(2); C(1)–C(2)–C(3) 119.4(1), C(2)–C(3)–C(4) 120.9(2), C(3)–C(4)–C(5) 120.2(2), C(4)–C(5)–C(6) 119.5(2), C(5)–C(6)–C(1) 121.8(2), C(6)–C(1)–Si(1) 117.8(1), C(2)–C(1)–Si(1) 124.1(1), C(1)–Si(1)–F(1) 108.3(1), C(1)–Si(1)–C(1) 110.6(1), C(2)–C(1)–C(7) 120.5(1), C(1)–C(2)–C(8) 126.6(2).

Crystal structure of tris(2-(2-dichloromethylsilyl)ethyl)phenylfluorosilane (20)

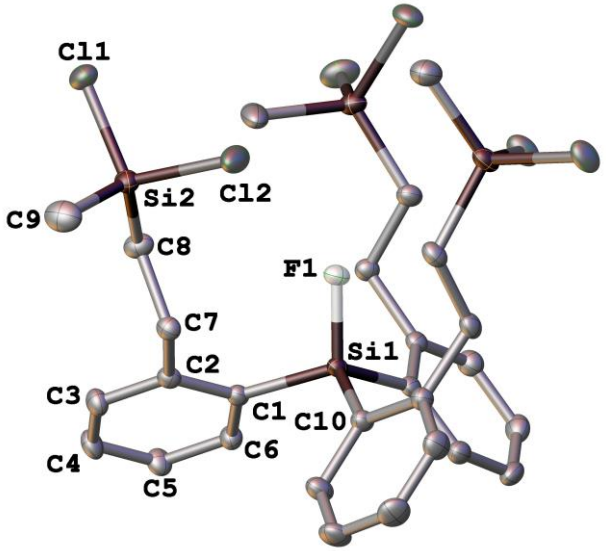

Figure S16 Molecular structure of tris(2-(2-dichloromethylsilyl)ethyl)phenylfluorosilane (**20**). Displacement ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [deg]: C(1)–C(2) 1.408(2), C(2)–C(3) 1.397(2), C(3)–C(4) 1.386(2), C(4)–C(5) 1.383(2), C(5)–C(6) 1.388(2), C(1)–C(6) 1.403(2), C(1)–Si(1) 1.867(1), Si(1)–F(1) 1.611(1), C(2)–C(7) 1.511(2), C(7)–C(8) 1.537(2), C(8)–Si(2) 1.841(1), Si(2)–Cl(1) 2.052(1), Si(2)–C(9) 1.828(2); C(1)–C(2)–C(3) 119.5(1), C(2)–C(3)–C(4) 121.1(1), C(3)–C(4)–C(5) 120.0(1), C(4)–C(5)–C(6) 119.5(1), C(5)–C(6)–C(1) 121.8(1), C(6)–C(1)–Si(1) 118.6(1), C(1)–Si(1)–F(1) 107.9(1), C(1)–Si(1)–C(10) 110.4(1), C(1)–C(2)–C(7) 123.0(1), C(2)–C(7)–C(8) 110.3(1), C(7)–C(8)–Si(2) 115.2(1), C(8)–Si(2)–C(9) 116.9(1), C(8)–Si(2)–Cl(1) 107.3(1), Cl(1)–Si(2)–C(9) 108.1(1).

Crystal structure of tris(2-(2-difluoromethylsilyl)ethyl)phenylfluorosilane (21)

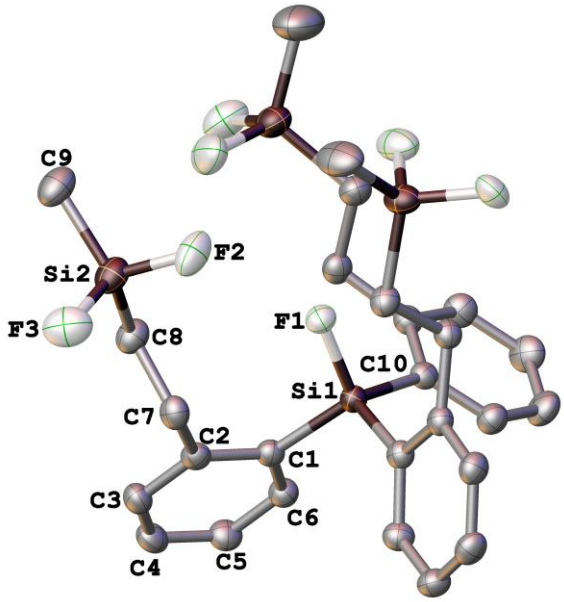

Figure S17 Molecular structure of tris(2-(2-difluoromethylsilyl)ethyl)phenylfluorosilane (**21**). Displacement ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [deg]: C(1)–C(2) 1.407(3), C(2)–C(3) 1.400(3), C(3)–C(4) 1.385(4), C(4)–C(5) 1.385(4), C(5)–C(6) 1.388(3), C(1)–C(6) 1.404(3), C(1)–Si(1) 1.874(2), Si(1)–F(1) 1.607(1), C(2)–C(7) 1.510(3), C(7)–C(8) 1.537(4), C(8)–Si(2) 1.845(3), Si(2)–F(2) 1.606(2), Si(2)–C(9) 1.823(3); C(1)–C(2)–C(3) 119.1(2), C(2)–C(3)–C(4) 121.4(2), C(3)–C(4)–C(5) 119.8(2), C(4)–C(5)–C(6) 119.7(2), C(5)–C(6)–C(1) 121.5(2), C(6)–C(1)–Si(1) 117.9(2), C(1)–Si(1)–F(1) 108.0(1), C(1)–Si(1)–C(10) 108.3(1), C(1)–C(2)–C(7) 122.7(2), C(2)–C(7)–C(8) 111.7(2), C(7)–C(8)–Si(2) 114.5(2), C(8)–Si(2)–C(9) 117.1(1), C(8)–Si(2)–F(2) 108.1(1), F(2)–Si(2)–C(9) 109.1(1).

Diffusion NMR Experiments

a) General Remarks

^{19}F Diffusion NMR measurements have been performed on a Bruker *Avance 600* instrument in C_6D_6 at 294 K using the LED sequence with bipolar gradients (ledbpgp2s) delivered by the manufacturer. The diffusion delay time (big delta, Δ) has been set to 80 ms for each compound. The probe was disconnected from the gas supply and the sample was allowed to equilibrate for at least three hours within the probe/magnet prior to data recording. The duration of the gradients (little delta, δ) has been adjusted between 3.2 ms (**17**) and 5.0 ms (**14**+**17**) and was incremented linearly in 16 steps. All measurements have been performed using a triple resonance probe with a maximum gradient strength of 5.57 G*cm^{-1}*A^{-1}. The diffusion coefficients have been calculated by using the relaxation module of the Bruker software TOPSPIN®. The three measured compounds were observed by their resonances in the ^{19}F NMR spectra.

b) Results

Table S5: Results of the DOSY-NMR measurements in C_6D_6 at 25 °C.

Compound	Diff coeff. [10^{-10} m^2/s]	M_w [g/mol]
11	5.358	566
17	7.793	249
TSCH[S5]	7.190	462
Adamantane[S6]	14.27	136
Si(Me)$_4$[S6]	18.00	88
14 + **17**	2.953	1557

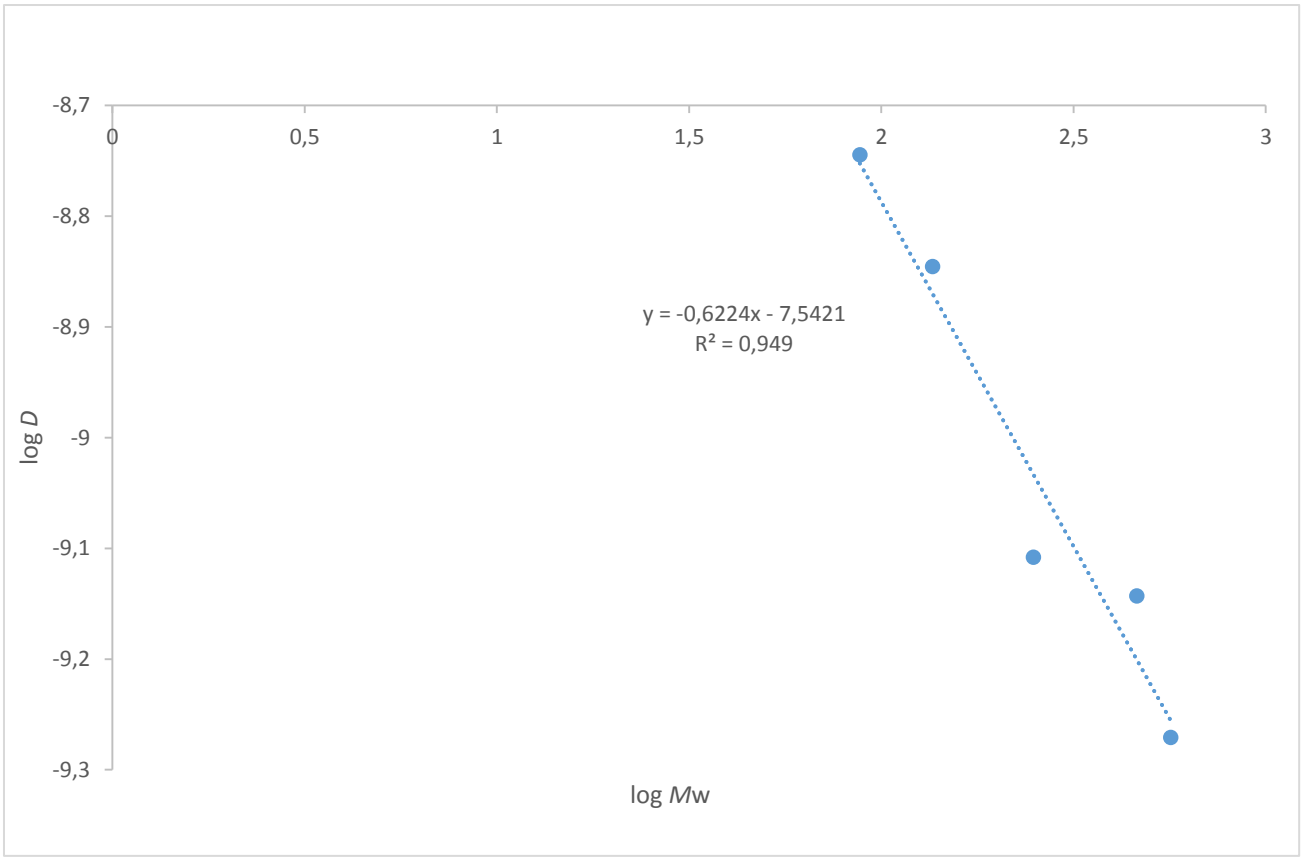

Figure S18 Logarithmic diffusion coefficients *D* plotted against the logarithmic molecular weight of model compounds **11**, **17** and external standards 1,3,5-tris(trimethylsilylethynyl)-1,3,5-trimethyl-1,3,5-trisilacyclohexane,[S5] $Si(Me)_4$[S6] and adamantane[S6].

References

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