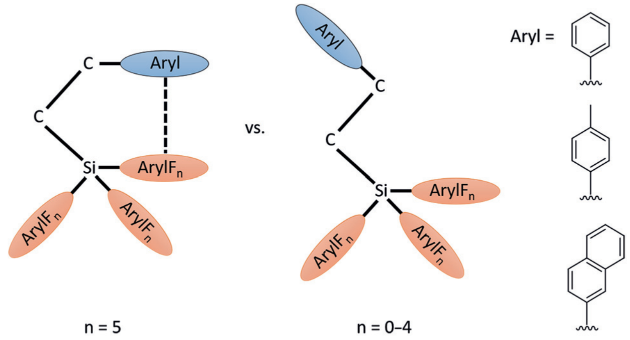
Synthesis and Structural Diversity of Triaryl(phenylethyl)silanes

Marvin Linnemannstöns
Beate Neumann
Hans-Georg Stammler
Norbert W. Mitzel*

Universität Bielefeld, Fakultät für Chemie,
Lehrstuhl für Anorganische Chemie und
Strukturchemie, Universitätsstraße 25,
33615 Bielefeld, Germany
mitzel@uni-bielefeld.de



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Abstract Starting from trichloro(phenylethyl)silane, six differently fluorinated triaryl(phenylethyl)silanes were synthesized by salt elimination reactions and their structures were determined by X-ray diffraction analysis. Tris(pentafluorophenyl)(phenylethyl)silane reveals a folded structure due to intramolecular π-stacking interactions, while those with a lower degree of fluorination show either intermolecular π-stacking or no interplay between the aryl groups. A similar folded structure was observed for (4-methylphenethyl)tris(pentafluorophenyl)silane and [2-(naphth-2-yl)ethyl]tris(pentafluorophenyl)silane, both generated from the corresponding trichlorosilanes. In contrast, the inversely fluorinated [2-(pentafluorophenyl)ethyl]triphenylsilane only revealed intermolecular π-stacking interactions. Compounds with tetrafluoropyridyl substituents behave differently; with these compounds, π-stacking is only observed between the fluorinated units. All compounds were analyzed by NMR and IR spectroscopy, elemental analyses and single-crystal X-ray diffraction, and found to have strong H/C/N/F···F and N···C contacts.

Key words inter/intramolecular π-stacking, solid-state structures, London dispersion, bridged arenes, fluorinated arenes

The first report on the interactions between fluorinated and non-fluorinated arenes was published by Patrick and Prosser in 1960.[1] They obtained colorless crystals by mixing equimolar amounts of benzene (C_6H_6; mp 6 °C) and hexafluorobenzene (C_6F_6; mp 4 °C). The melting point of this 1:1 complex was 24 °C and thus about 19 °C higher than those of the individual components. In contrast to the herringbone-like relative arrangements of the molecules in the crystal structures of pure C_6H_6 and C_6F_6,[2] the co-crystal $C_6H_6{\cdot}C_6F_6$ consists of columnar stacks of alternating benzene and hexafluorobenzene molecules.[3] First attempts to explain this phenomenon were based on the interaction between the quadrupolar moments of C_6H_6 and C_6F_6, which are of equal magnitude but of opposite sign.[4] Later investigations revealed that London dispersion has at least the same impact on the total interaction energy as the electrostatic term.[5] Intermolecular interactions involving aromatic rings play an important role in many supramolecular recognition processes;[6] for example, in the intercalation of drugs to DNA,[7] in host-guest complexation,[8] and in crystal engineering.[9] The creation of a toolbox with specific molecular building blocks that induce a particular kind of inter- or intramolecular interactions in a system would be a great benefit for synthetic chemists in the development and design of new molecules. Recently, we reported on the structural characteristics of partially fluorinated bis-arenes in the solid and the gas phase.[10] $H_5C_6{-}(CH_2)_2SiMe_2{-}C_6F_5$ contains a $-(CH_2)_2SiMe_2-$ linker unit connecting a phenyl and a pentafluorophenyl group. The existence of two conformers was detected by gas-phase electron diffraction (GED). The most abundant conformer (**A**) is stabilized by intramolecular π-stacking, while the other one (**B**) is stabilized by σ–π interactions (Figure 1). This led us to the question of whether substitution of the two methyl groups with further pentafluorophenyl moieties would suppress the σ–π conformer and exclusively lead to the structure stabilized by intramolecular π-stacking interactions.

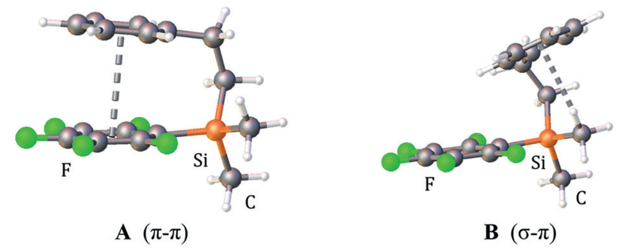

Figure 1 Structures of the π–π (**A**) and the σ–π conformer (**B**) of dimethyl(pentafluoro)(2-phenylethyl)silane determined by GED[10]

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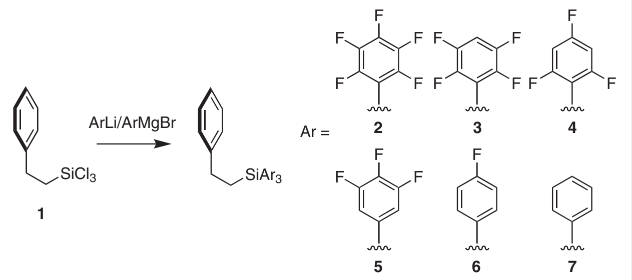
Herein, we report the synthesis and structural characteristics of several tris(aryl)(phenylethyl)silanes (TAPS) with varying degrees of fluorination; in particular with respect to the occurrence of inter- vs. intramolecular π-stacking.

The syntheses of different fluorinated TAPS by salt elimination reactions of trichloro(phenylethyl)silane with the corresponding lithiated arenes are shown in Scheme 1. Purification by column chromatography and recrystallization from *n*-hexane afforded colorless solids. The six new TAPS were obtained in moderate to good yields. They were characterized by multinuclear NMR spectroscopy, elemental analyses and by single-crystal X-ray diffraction. Note that silanes **2**–**7** are insensitive towards moisture and can be stored under atmosphere for at several months without decomposition.



Scheme 1 Synthesis of the tris(aryl)(phenylethyl)silanes via salt elimination reactions of trichloro(phenylethyl)silane with the corresponding lithiated arenes. Yields: 85% (**2**), 61% (**3**), 48% (**4**), 68% (**5**), 78% (**6**), 92% (**7**).

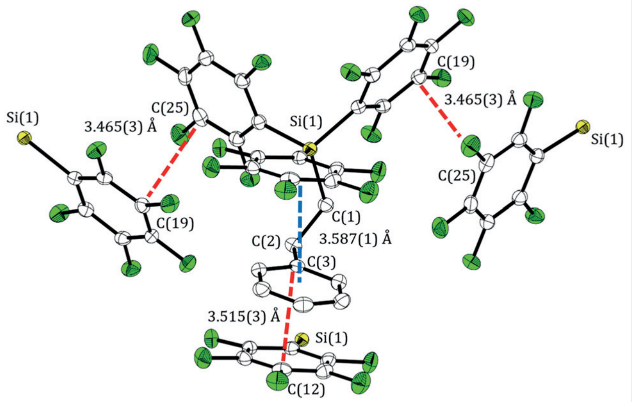


Figure 2 Molecular structure and primary aggregation of **2** in the crystalline state with an intramolecular centroid–centroid distance of 3.587(1) Å. Displacement ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity.

Single crystals suitable for X-ray diffraction experiments of compounds **2**–**7** were obtained upon slow evaporation of the solvent of saturated *n*-hexane solutions. TAPS **2** crystallizes in the monoclinic group $P2_1/n$ with four molecules per unit cell. Figure 2 illustrates this pentafluorophenyl substituted silane **2** and reveals a folded structure stabilized by intramolecular π-stacking interactions with a centroid–centroid distance $d_{\mathrm{centroids}}$ of 3.587(1) Å. The interacting aryl groups are almost coplanar [angle between their mean planes: 9.73(4)°]. However, no π-stacking to neighboring molecules is observed, whereas short intermolecular distances C(19)···C(25) at 3.465(3) Å and C(3)···C(12) at 3.515(3) Å are found, which are slightly above the sum of the van der Waals (vdW) radii. The coordination geometry at the silicon atom is almost tetrahedral ($\tau_4 = 0.96$). The presence of many fluorine atoms leads to C···C and F···F contacts in the crystal structure. The shortest C···F contact was found for the pair C(24)···F(4) [2.950(1) Å]. The shortest F···F contact occurred between the pair F(1)···F(9) [2.796(1) Å]. Similar results were reported by Dilman et al.[11] In 2005 they presented the synthesis of several methylene bridged tris(pentafluorophenyl)silanes and observed a folded structure for benzyltris(pentafluorophenyl)silane.

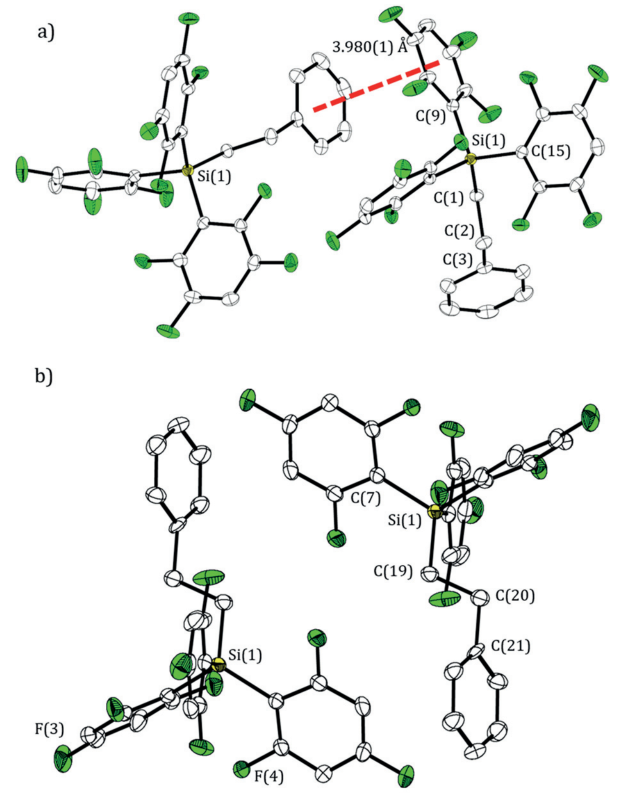


Figure 3 (a) Molecular structure and primary aggregation of **3** in the crystalline state with an intermolecular centroid–centroid distance of 3.980(1) Å. (b) The tilted T-like arrangement of compound **4**. Displacement ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity.

In contrast to compound **2**, TAPS **3**–**7** crystallize in stretched conformations stabilized by different interactions. Substitution of the *p*-fluorine with a hydrogen atom exclusively leads to a stretched conformation [ϕSi(1)–C(1)–

Table 1 Selected Structural Parameter of Silanes **2–7**, **10**, **11**, **13**, **15** and **16**

Entry	Structure[a]	X[b]	ϕ(SiCCC) [°]	τ_4	d_{c-c}inter [Å]	d_{c-c}intra [Å]	H···F [Å]	C···C [Å]	C···F [Å]	F···F [Å]	N···C [Å]	N···F [Å]
2	f	1	76.8(1)	0.96	–	3.587(1)	2.5(1)	3.465(3)	2.950(1)	2.796(1)	–	–
3	s	1	176.1(1)	0.96	3.980(1)	–	2.4(2)	3.395(2)	3.092(2)	2.853(1)	–	–
4	s	1	171.6(3)	0.96	–	–	2.5(1)	3.303(3)	3.125(2)	2.798(2)	–	–
5	s+f	5	75.9(3)–178.7(1)	0.99–0.95	3.670(1)–3.955(2)	3.700(2)	2.3(1)	3.279(6)	2.896(4)	2.705(1)	–	–
6	s	2	166.3(1)–175.3(1)	0.99–0.98	–	–	2.6(1)	3.284(3)	3.117(2)	–	–	–
7	s	1	175.1(1)	0.97	–	–	–	3.352(3)	–	–	–	–
10	s	2	148(5)–28(3)	0.96–0.95	3.473(1)–3.922(1)	–	2.6(2)	3.290(2)	3.196(2)	2.769(1)	–	–
11	s	1	171.2(1)	0.97	3.701(1)	–	2.4(1)	3.360(2)	2.995(1)	2.876(2)	–	–
13	f	1	80.3(2)	0.97	–	3.714(1)	2.5(1)	3.261(2)	3.014(2)	2.765(1)	–	–
15	f	1	73.4(2)	0.97	–	3.465(1)	2.6(1)	3.305(3)	2.997(2)	2.631(2)	–	–
16	s	2	176.5(1)–179.2(1)	0.94	3.660(1)	–	2.5(1)	3.323(2)	2.948(2)	2.912(2)	3.097(2)	2.935(2)

[a] s: stretched; f: folded.
[b] X: molecules per asymmetric unit.

C(2)–C(3) = 176.1(1)°] (Figure 3a). In contrast to the pentafluorophenyl derivative **2**, TAPS **3** features a dimeric structure stabilized by intermolecular π-stacking. Compared with compound **2**, the resulting distance of the mean planes [$d_{\text{centroids}}$ = 3.980(1) Å] is somewhat larger. As detected for the pentafluorophenyl derivative, many F···F, H···F, C···C, and C···F contacts are observed; the shortest are summarized in Table 1. The coordination geometry at the silicon atom is almost tetrahedral (τ_4 = 0.96).

Compound **4** contains only three fluorine atoms per phenyl group in a 2,4,6-substitution pattern. In contrast to compound **3**, the stretched molecular structure of TAPS **3**

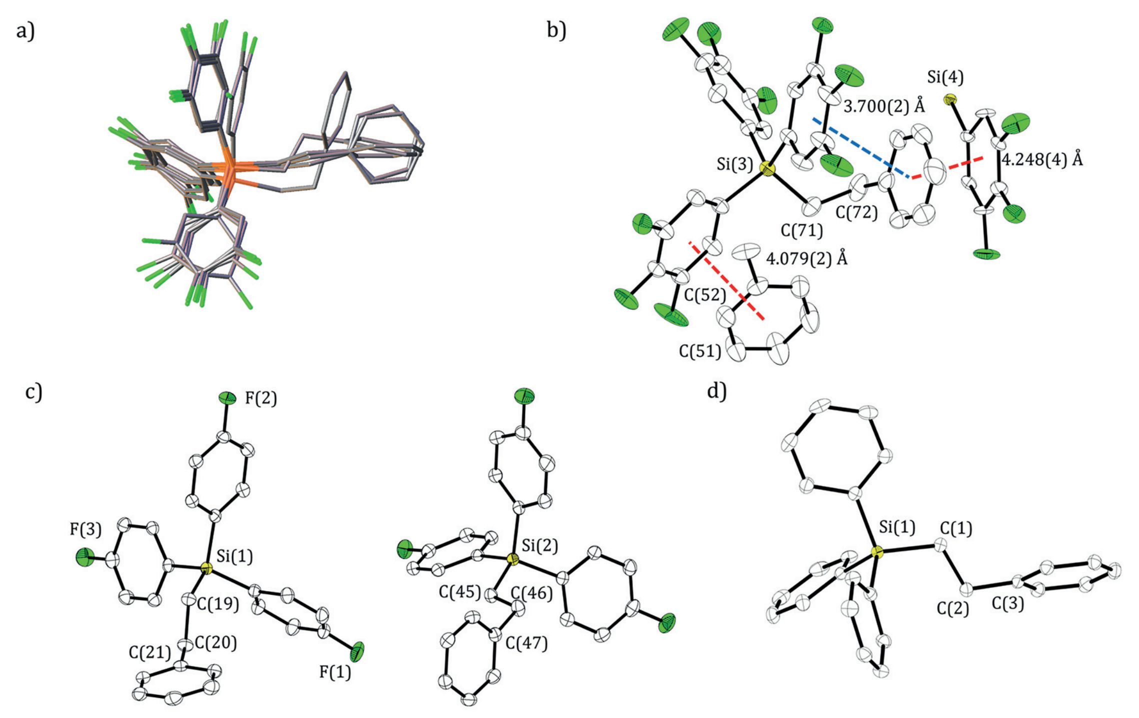


Figure 4 (a) Overlay of the five independent molecules of TAPS **5** revealing one folded and four stretched structures in the asymmetric unit. (b) Fragment of the asymmetric unit of compound **5** revealing the folded structure and its primary aggregation with centroid–centroid distances ranging from 3.700(2) to 4.248(4) Å. (c) Asymmetric unit of compound **6** in the crystalline state, revealing a stretched structure without π-stacking. (d) Molecular structure of silane **7**. Displacement ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity.

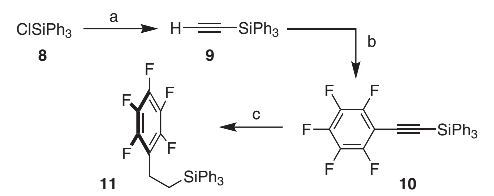
[ϕSi(1)–C(19)–C(20)–C(21) = 171.6(3)°] reveals no intramolecular π-stacking interactions (Figure 3b). However, the tilted T-like arrangement of TAPS **4** dimers resembles somewhat the molecular structure of pure benzene. Still the structure of **4** is dominated by several short H/C/F···F and C···C contacts (Table 1).

To assess whether there is a structural difference depending on whether the fluorine atoms are distributed evenly or half-sided at the fluorinated phenyl groups, the crystal structure of TAPS **5** was examined. In contrast to the previously discussed compounds, this 3,4,5-trifluorophenyl substituted silane **5** crystallizes with five molecules per asymmetric unit (Figure 4a).

While four molecules reveal an overall stretched conformation [ϕSi–C–C–C$_{\text{phenyl}}$ = 167.1(2)–178.7(1)°], one shows intramolecular π-stacking interactions and a folded structure [ϕSi(1)–C(19)–C(20)–C(21) = 75.9(3)°] (Figure 4b). Compared to TAPS **2**, the intramolecular distance of the centroids is slightly longer [$d_{\text{centroids}}$ = 3.700(2) Å], while the planes deviate more from co-planarity [angle between their mean planes: 6.6(1)°] but are less twisted [9.3(2)°]. π-Stacking to neighboring molecules occurs for the folded structure, but only with relatively long distances between the centroids [$d_{\text{centroids}}$ = 4.079(2)–4.248(4) Å]. The four independent molecules are mainly stabilized by intermolecular π-stacking interactions, with centroid–centroid distances ranging from 3.670(1) Å to 3.955(2) Å and short H/C/F···F and C···C contacts (Table 1). The coordination geometry at all silicon atoms is almost tetrahedral (τ_4 = 0.95–0.99).

The 4-fluorophenyl substituted compound **5** (Figure 4c) and the non-fluorinated TAPS **7** (Figure 4d) both reveal no π-stacking interactions to neighboring molecules, but a tilted T-like arrangement. In contrast to the compounds with a higher degree of fluorination, **6** reveals short H/C···F and C···C contacts but no F···F interactions.

Whereas only silane **2** and partially TAPS **5** feature folded structures, we wanted to investigate this phenomenon for the inversely fluorinated case. We therefore generated [(pentafluorophenyl)ethyl]triphenylsilane (**11**) in a three-step synthesis (Scheme 2). Starting from chlorotriphenylsilane (**8**), ethynyltriphenylsilane (**9**) was obtained by using a modification of a reported procedure.[12] The pentafluorophenyl group was introduced by Sonogashira coupling. Subsequent palladium-catalyzed reduction of the alkyne unit with hydrogen afforded the ethylene linking unit.



Scheme 2 Synthesis of ethynyltriphenylsilane (**9**), ethynyl[(pentafluorophenyl)ethynyl]triphenylsilane (**10**), and [(pentafluorophenyl)ethyl]triphenylsilane (**11**). *Reagents and conditions*: (a) ethynylmagnesium bromide (0.5 M in THF), THF, 65 °C, 1 h, 65% (Lit.[12] 68%); (b) C_6F_5Br, HN^{i}Pr$_2$, CuI, Pd(PPh$_3$)$_4$, THF, 60 °C, 2 d, 89%; (c) H$_2$, Pd/C, DCM, r.t., 4 h, 81%.

The molecular structures of silanes **10** and **11** were determined by X-ray diffraction analysis of suitable single crystals, which were grown from solution by slow evaporation of the solvent (n-hexane). Compound **10** crystallizes in the monoclinic space group $P2/n$ with eight molecules per unit cell (Figure 5). The asymmetric unit comprises two independent molecules with very similar structures. The chain-like structures are stabilized by π-stacking interactions, but unlike TAPS **2**, **3**, and **5**, not only by an interplay of a fluorinated and a non-fluorinated aryl group [$d_{\text{centroids}}$ = 3.878(1) and 3.922(1) Å]. Instead π-stacking of two C_6F_5 moieties [$d_{\text{centroids}}$ = 3.473(1) and 3.522(1) Å] is observed; these distances are about 0.4 Å shorter than in the C_6H_5–C_6F_5 stacks. All C≡C–Si/ C≡C–C$_{\text{Ar}}$ units [d(C≡C) = 1.198(2)–1.203(2) Å] deviate slightly from linearity; the corresponding C≡C–Si and C≡C–C$_{\text{Ar}}$ angles range from 173.8(2)° [Si(2)–C(27)–C(28)] to 178.7(1)° [C(1)–C(2)–C(3)]. We found earlier that this is a typical range for this type of compounds in

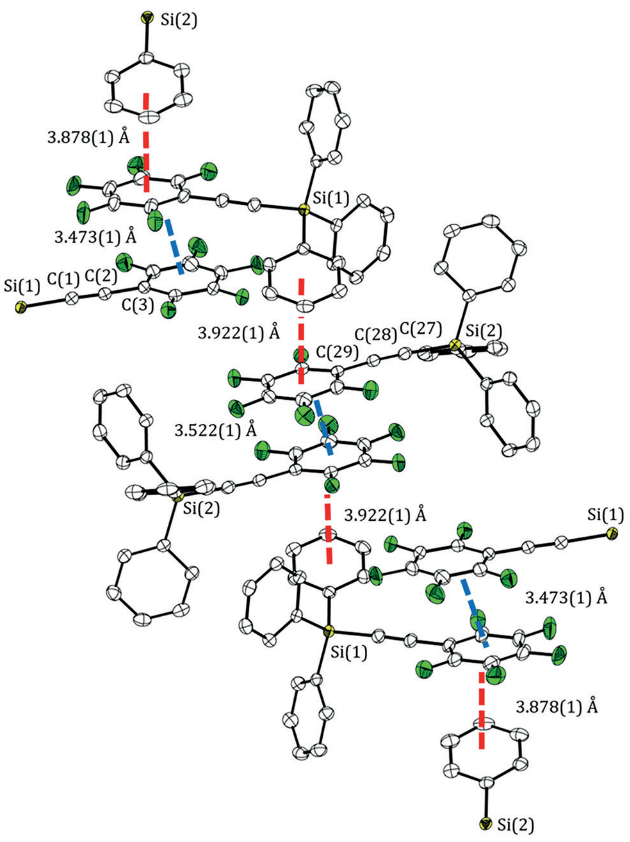


Figure 5 Molecular structure and aggregation of **10** in the crystalline state with centroid–centroid distances ranging from 3.473(1) Å to 3.922(1) Å. Displacement ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity.

the solid state.[13] As already observed for other fluorinated TAPS, the molecule seeks additional stabilization by H/F···F contacts.

The molecular structure of the hydrogenated species **11** is depicted in Figure 6. All bond lengths and angles are found to be in the expected ranges. In contrast to its inversely fluorinated counterpart **2**, the structure of **11** in the crystal is not folded [ϕSi(1)–C(19)–C(20)–C(21) = 171.2(3)°], but receives stabilization by intramolecular π-stacking interactions [$d_{\text{centroids}}$ = 3.701(1) Å]; this leads to the formation of dimeric structures. The opposing aryl groups are folded by 9.9(1)° and twisted by 38.2(2)° to each other. However, no pronounced π-stacking to neighboring dimers is observed, but remarkably short H/C/F···F contacts are noted, with some being below the sum of the van der Waals radii (Table 1).

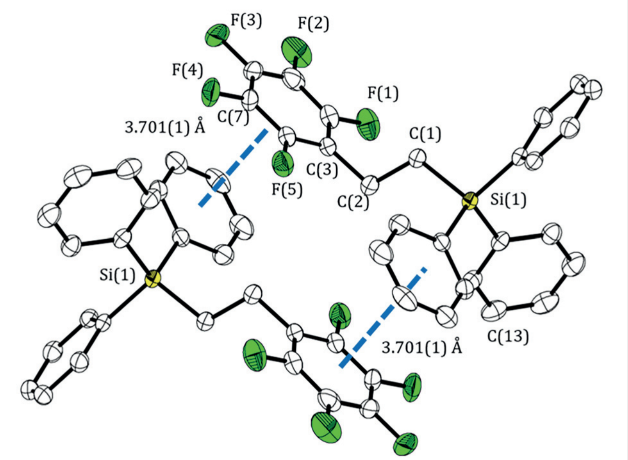
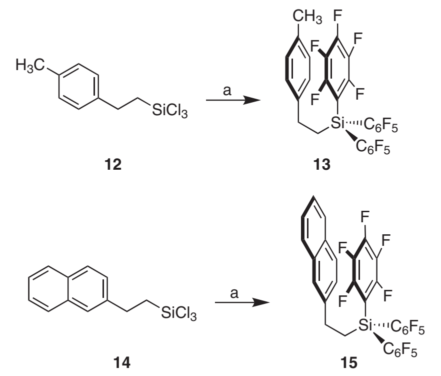


Figure 6 Molecular structure and aggregation of **11** in the crystalline state with an intramolecular centroid–centroid distance of 3.701(1) Å. Displacement ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity.

To date, it seems that only compounds with a tris(pentafluorophenyl)silyl group linked by an ethylene unit to a phenyl ring offer folded structures in the crystalline state. By varying the phenyl unit with other aromatic groups, we wanted to investigate the structural properties of the resulting silanes. As shown in Scheme 3, two tris(pentafluoro)phenyl-substituted TAPS were synthesized, bearing a 4-tolyl (**13**) or a 2-naphthyl (**15**) group. The synthesis of the trichlorosilane precursors **12** and **14** was published by Wang et al.[14] The introduction of the pentafluorophenyl groups as well as the purification and isolation process are analogous to those of TAPS **2**–**7**.



Scheme 3 Synthesis of (4-methylphenethyl)tris(pentafluorophenyl)silane (**13**) and [2-(naphth-2-yl)ethyl]tris(pentafluorophenyl)silane (**15**) starting from the corresponding trichlorosilanes **12** or **14**. *Reagents and conditions*: (a) bromopentafluorobenzene, *n*-butyllithium (1.6 M in *n*-hexane), diethyl ether, –78 °C (1 h) to r.t. (12 h), 82% (**13**), 76% (**15**).

Compound **13** crystallizes in the triclinic space group $P\bar{1}$ (Figure 7) with two molecules per unit cell and reveals a folded structure [ϕSi(1)–C(1)–C(2)–C(3) = 80.3(2)°]. Compared to silane **2**, the centroid–centroid distance of the interacting aryl moieties with $d_{\text{centroids}}$ = 3.714(1) Å is slightly longer and the angles between the mean planes are wider [8.1(1)°]. This may be due to the steric demand of the methyl groups. As observed for TAPS **2**, no pronounced intermolecular π-stacking to neighboring molecules occurs, but remarkably short interatomic distances are detected. For instance, these strong contacts arise between C(18)···C(19) [d = 3.261(1) Å], and C(7)···C(12) [d = 3.481(2) Å], with the first distances being below the sum of the corresponding van der Waals radii and are slightly shorter than the contacts observed for compound **2**.

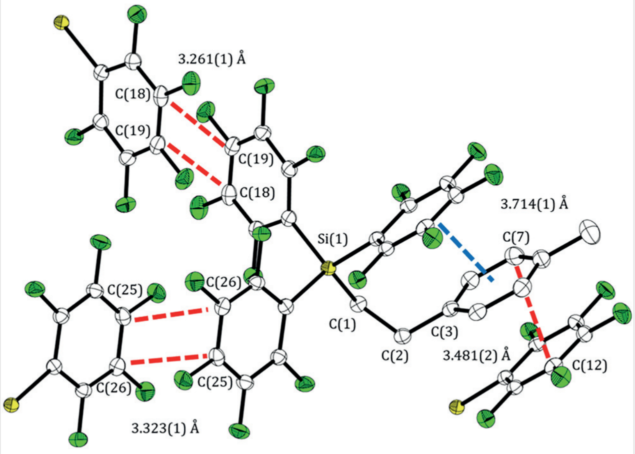


Figure 7 Molecular structure and primary aggregation of **13** in the crystalline state with an intramolecular centroid–centroid distance of 3.714(1) Å. Displacement ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity.

The molecular structure of the naphthyl substituted TAPS **15** (Figure 8) is very similar to both tris(pentafluoro)phenylsilyl functionalized systems, **2** and **13**. As indicated by the torsion angle ϕSi(1)–C(19)–C(20)–C(21) at 73.4(2)° the structure features a folded conformation. The result is a remarkably short centroid–centroid distance between the mean planes of C(13)–C(14)–C(15)–C(16)–C(17)–C(18) and C(3)–C(4)–C(5)–C(10)–C(11)–C(12) of 3.465(1) Å, which is significantly shorter than the distances observed in **2** and **13**. In comparison to the compounds discussed above, this structure contains no significant intermolecular π-stacking interaction, even though the naphthyl group offers enough surface area for further interactions. As indicated by the torsion angles ϕC(3)–C(4)–C(5)–C(6) at 173.3(2)° and ϕC(9)–C(10)–C(11)–C(12) at 175.8(2)° the naphthyl unit suffers a distortion from planarity, which may arise from the π-stacking interaction.

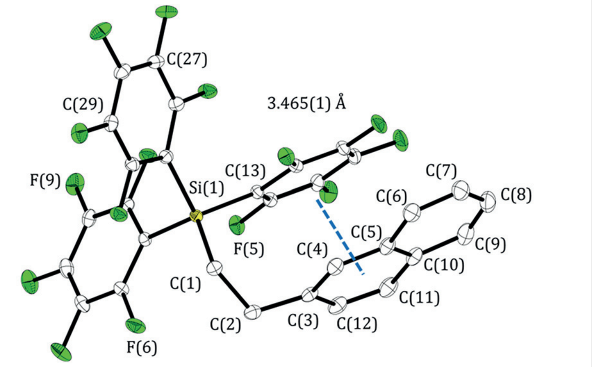
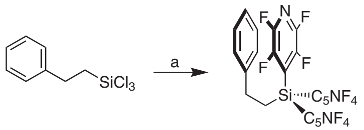


Figure 8 Molecular structure of **15** in the crystalline state with an intramolecular centroid–centroid distance of 3.464(1) Å. Displacement ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity.

Since only the pentafluorophenyl substituted silanes lead to folded structures, the question arose, whether perfluorinated heteroaromatics would lead to similar structures. Recently, Schwabedissen et al. investigated the structure of several 1:1 co-crystals containing *p*-halotetrafluoropyridines and benzene.[15] They showed that the columnar structures had high similarities to the co-crystal $C_6H_6{\cdot}C_6F_6$.[1] As depicted in Scheme 4, we consequently synthesized the tetrafluoropyridyl substituted TAPS **16** by salt elimination starting from chlorosilane **2**. This is, to our knowledge, the first known tris(2,3,4,5-tetrafluoropyridyl)silane derivative reported to date. In contrast to the TAPS presented, TAPS **16** seems to be labile towards moisture. This is probably due to the stronger electron-withdrawing character of the tetrafluoropyridyl substituent compared to C_6F_5.[16]



1 **16**

Scheme 4 Synthesis of (phenylethyl)tris(2,3,4,5-tetrafluoropyridyl)silane (**16**) starting from trichlorophenylethylsilane (**1**). *Reagents and conditions*: (a) tetrafluoropyridine, *n*-butyllithium (1.6 M in *n*-hexane), DE, −78 °C (4 h) to r.t. (12 h), 78%.

Compound **16** crystallizes in the triclinic space group $P\bar{1}$ with four molecules per unit cell (Figure 9). The asymmetric unit consists of two molecules, both featuring a stretched conformation [ϕSi(1)–C(1)–C(2)–C(3) at 176.5(1)° and ϕSi(2)–C(24)–C(25)–C(26) at 179.2(1)°]. In contrast to the trispentafluorophenylsilyl-substituted compounds, **16** does not reveal intramolecular π-stacking. Instead intermolecular π-stacking interactions of two NC_4F_4 groups [$d_{\text{centroids}}$ = 3.660(1) Å] are found. In addition, remarkably short H/C/N/F···F and N···C contacts are observed. The strongest contacts of each kind are below the sum of the van der Waals radii (Table 1).

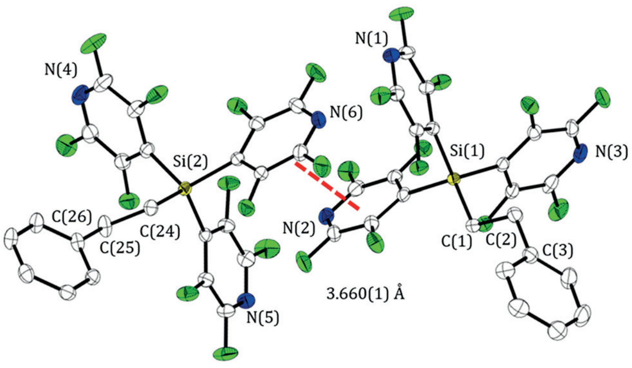


Figure 9 Molecular structure of **16** in the crystalline state. Displacement ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity.

In conclusion, a series of trisaryl(arylethyl)silanes was synthesized and investigated regarding their molecular structures in the crystalline state. By varying the degree of fluorination and using the flexible C–C–Si linking unit, different structural motifs were observed. Intramolecular π-stacking and an associated folded structure are observed for compounds with tris(pentafluorophenyl)silyl groups. Successive reduction of the number of fluorine atoms consistently leads to stretched structures. However, for the inversely fluorinated ([pentafluorophenyl]ethyl)triphenylsilane no analogous result is observed. The molecular structure in the crystalline state of a tetrafluoropyridyl functionalized system is dominated by strong H/C/N/F···F and N···C contacts and does not reveal any prominent π-stacking at all.

1-Bromo-2,3,4,5,6-pentafluorobenzene, 1-bromo-3,4,5-trifluorobenzene, 1,2,4,5-tetrafluorobenzene, 1,3,6-trifluorobenzene, 1-bromo-4-fluorobenzene, 2,3,5,6-tetrafluopyridine, CuI, tetrakis(triphenylphosphane)palladium(0) (all purchased from Fluorochem), *n*-butyllithium (1.6 M in *n*-hexane), 1-bromobenzene (both from Arcos Organics), ethynylmagnesium bromide (0.5 M in THF from Fisher Scientific), chlorotriphenylsilane (from TCI) and Mg turnings (from Merck) were used without further purification. All reactions using metal organic reagents were carried out under a dry atmosphere of N_2 using standard Schlenk techniques in anhydrous diethyl ether (DE) or THF (dried over $LiAlH_4$ or K and freshly distilled before use). Column chromatography was performed on silica gel 60 (0.040–0.063 mm). NMR spectra were recorded with a Bruker Avance 300, a Bruker DRX 500, or a Bruker Avance III 500 instrument at 298 K and referenced to solvent ($CDCl_3$: ^1H NMR δ = 7.26 ppm, ^{13}C NMR δ = 77.16 ppm; C_6D_6: ^1H NMR δ = 7.16 ppm, ^{13}C NMR δ = 128.06 ppm) or referenced externally (^{29}Si NMR: TMS). Elemental analyses were performed with a Euro EA Elemental analyzer. EI mass spectra were recorded with an AutospecX magnetic sector mass spectrometer with EBE geometry (Vacuum Generators, Manchester UK) equipped with a standard EI source; samples were introduced with a push rod in aluminum crucibles; ions were accelerated by 8 kV.

Introduction of Arenes by Lithiation; General Procedure

The corresponding HAr/BrAr was dissolved in diethyl ether and cooled to –78 °C. A syringe was used to slowly add *n*-butyllithium (1.6 M in *n*-hexane, 1 equiv). After complete addition, the reaction mixture was stirred for 1 h. The respective trichlorosilane was then added at –78 °C by using a syringe and the solution was slowly heated to r.t. overnight. After hydrolyzing with water and extraction of the aqueous layer with CH_2Cl_2, the combined organic phases were dried with Na_2SO_4. The solvent was removed under reduced pressure and the crude product was purified by column chromatography on silica gel and subsequent crystallization.

Tris(pentafluorophenyl)(phenylethyl)silane (2)

Prepared according to the General Procedure using 1-bromo-2,3,4,5,6-pentafluorobenzene (1.6 mL, 13 mmol, 3 equiv), diethyl ether (100 mL), *n*-butyllithium (1.6 M in *n*-hexane, 7.9 mL, 13 mmol, 3 equiv) and trichloro(phenylethyl)silane (1.0 g, 4.2 mmol, 1 equiv). Column chromatography (*n*-pentane) and recrystallization from *n*-hexane afforded **2** as colorless crystals.

Yield: 2.3 g (3.6 mmol, 85%).

AT-IR: 3030, 2917, 2866, 1643, 1603, 1585, 1518, 1455, 1406, 1377, 1288, 1260, 1176, 1086, 997, 966, 928, 897, 851, 821, 760, 747, 729, 713, 697, 675, 631, 622, 602, 587, 570, 550, 520, 512, 483, 448, 440, 420 cm^{-1}.

^1H NMR (500 MHz, C_6D_6): δ = 7.11 (m, 2 H, ArH), 7.05 (m, 3 H, ArH), 2.62 (m, 2 H, CH_2Si), 1.91 (m, 2 H, CH_2Ph).

$^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6): δ = 149.5 (Ar–C_6F_5), 143.7 (Ar–C_6F_5), 142.5 (Ar–C_6H_5), 137.8 (Ar–C_6F_5), 129.0 (Ar–C_6H_5), 128.4 (Ar–C_6H_5), 126.8 (Ar–C_6H_5), 104.5 (Ar–C_6F_5), 29.7 (Ph–CH_2), 17.3 (Si–CH_2).

$^{19}F\{^1H\}$ NMR (470 MHz, C_6D_6): δ = 126.9 (m, 2 F, *o*-F), –146.5 (m, *p*-F), –159.5 (m, 2 F, *m*-F).

$^{29}Si\{^1H\}$ NMR (99 MHz, C_6D_6): δ = 23.5.

Anal. Calcd (%) for $C_{26}H_9F_{15}Si$: C, 49.22; H, 1.42. Found: C, 49.70; H, 1.43.

Phenylethyltris(2,3,5,6-tetrafluorophenyl)silane (3)

Prepared according to the General Procedure using 1,2,4,5-tetrafluorobenzene (1.3 mL, 13 mmol, 3 equiv), diethyl ether (100 mL), *n*-butyllithium (1.6 M in *n*-hexane, 7.9 mL, 13 mmol, 3 equiv) and trichloro(phenylethyl)silane (1.0 g, 4.2 mmol, 1 equiv). Column chromatography (*n*-pentane) and recrystallization from *n*-hexane afforded **3** as colorless crystals.

Yield: 2.5 g (2.6 mmol, 61%).

AT-IR: 3118, 3082, 3059, 3033, 2903, 2541, 1820, 1721, 1600, 1460, 1384, 1358, 1267, 1227, 1171, 1134, 1113, 1028, 1005, 901, 860, 853, 767, 723, 707, 693, 671, 573, 541, 522, 499, 449, 438, 428 cm^{-1}.

^1H NMR (500 MHz, C_6D_6): δ = 7.05 (m, 5 H, ArH), 6.20 (tt, $J_{F,H}$ = 9.2 Hz, $J_{F,H}$ = 7.1 Hz, 3 H, Ar_FH), 2.66 (m, 2 H, CH_2CH_2Si), 2.0 (m, 2 H, CH_2CH_2Si).

$^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6): δ = 149.2 (Ar–C_6HF_4), 146.1 (Ar–C_6HF_4), 143.0 (Ar–C_6H_5), 128.9 (Ar–C_6H_5), 128.1 (Ar–C_6H_5), 126.5 (Ar–C_6H_5), 111.2 (Ar–C_6F_5), 109.9 (Ar–C_6F_5), 29.8 (CH_2CH_2Si), 17.3 (CH_2CH_2Si).

$^{19}F\{^1H\}$ NMR (470 MHz, C_6D_6): δ = 127.6 (m), –137.2 (m).

$^{29}Si\{^1H\}$ NMR (99 MHz, C_6D_6): δ = 23.3.

MS (EI, 70 eV): *m*/*z* = 580.1 $[M]^+$, 431.1 $[M - C_6HF_4]^+$.

HRMS: *m*/*z* calcd for $C_{26}H_{12}F_{12}Si^+$: 580.05112; found: 580.05277.

Anal. Calcd (%) for $C_{26}H_{12}F_{12}Si$: C, 53.80; H, 2.08. Found: C, 53.91; H, 2.09.

Phenylethyltris(2,4,6-trifluorophenyl)silane (4)

Prepared according to the General Procedure using 1,3,5-trifluorobenzene (1.3 mL, 13 mmol, 3 equiv), diethyl ether (100 mL), *n*-butyllithium (1.6 M in *n*-hexane, 7.9 mL, 13 mmol, 3 equiv) and trichloro(phenylethyl)silane (1.0 g, 4.2 mmol, 1 equiv). Column chromatography (*n*-pentane) and recrystallization from *n*-hexane afforded **4** as colorless crystals.

Yield: 1.1 g (2.0 mmol, 48%).

AT-IR: 3101, 3066, 3029, 2935, 1688, 1626, 1601, 1578, 1514, 1496, 1475, 1455, 1408, 1325, 1282, 1177, 1161, 1117, 1090, 1069, 1010, 999, 894, 840, 760, 733, 693, 640, 617, 585, 572, 558, 514, 490, 463, 439, 418 cm^{-1}.

^1H NMR (500 MHz, C_6D_6): δ = 7.15 (m, 4 H, ArH), 7.06 (m, 1 H, ArH), 6.16 (m, 3 H, Ar_FH), 2.79 (m, 2 H, CH_2CH_2Si), 2.09 (m, 2 H, CH_2CH_2Si).

$^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6): δ = 167.6 (Ar–$C_6H_2F_3$), 165.6 (Ar–$C_6H_2F_3$), 144.3 (Ar–C_6H_5), 128.9 (Ar–C_6H_5), 128.2 (Ar–C_6H_5), 126.3 (Ar–C_6H_5), 105.3 (Ar–$C_6H_2F_3$), 100.5 (Ar–$C_6H_2F_3$), 30.3 (CH_2CH_2Si), 18.3 (CH_2CH_2Si).

$^{19}F\{^1H\}$ NMR (470 MHz, C_6D_6): δ = 94.0 (m), –103.9 (m).

$^{29}Si\{^1H\}$ NMR (99 MHz, C_6D_6): δ = 25.4.

MS (EI, 70 eV): *m*/*z* = 395.0 $[M - C_6H_2F_3]^+$.

Anal. Calcd (%) for $C_{26}H_{15}F_9Si$: C, 59.32; H, 2.87. Found: C, 59.11; H, 2.73.

Phenylethyltris(3,4,5-trifluorophenyl)silane (5)

To magnesium turnings (306 mg, 12.6 mmol, 3 equiv) in tetrahydrofuran (10 mL) a few drops of a solution of 1-bromo-3,4,5-trifluorobenzene (1.50 mL, 12.6 mmol, 3 equiv) in tetrahydrofuran (30 mL) were added until cloudiness and darkening showed the beginning of the Grignard reaction. The residual solution of 1-bromo-3,4,5-trifluorobenzene was added within 10 min and the reaction mixture was heated at reflux for 1 h until full consumption of magnesium was observed. At ambient temperature, trichloro(phenylethyl)silane (1.0 g, 4.2 mmol, 1 equiv) was added by using a syringe and the reaction mixture was heated at reflux for 1 h and stirred at r.t. overnight. After hydrolyzing with water (30 mL) and extraction of the aqueous layer with CH_2Cl_2 (3 × 50 mL), the combined organic phases were dried with Na_2SO_4. The solvent was removed under reduced pressure, resulting in the formation of a colorless oil, which was purified by column chromatography on silica gel to give a colorless solid. Crystallization from *n*-hexane afforded **5** as colorless crystals.

Yield: 1.5 g (2.9 mmol, 68%).

AT-IR: 3063, 3032, 2926, 2888, 2859, 2357, 1605, 1579, 1519, 1495, 1453, 1397, 1314, 1283, 1271, 1234, 1221, 1183, 1123, 1092, 1031, 905, 890, 856, 759, 746, 732, 712, 696, 681, 611, 611, 566, 530, 510, 489, 468, 432, 413 cm^{-1}.

^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.30 (m, 2 H, ArH), 7.15 (m, 2 H, ArH), 7.23 (m, 1 H, ArH), 7.03 (t $^2J_{F,H}$ = 6.7 Hz, 6 H, Ar$_F$H), 2.77 (m, 2 H, CH$_2$*CH*$_2$Si), 1.74 (m, 2 H, *CH*$_2$CH$_2$Si).

^{13}C {^{1}H} NMR (126 MHz, CDCl$_3$): δ = 151.8 (Ar–C$_6$H$_2$F$_3$), 142.8 (Ar–C$_6$H$_5$), 141.5 (Ar–C$_6$H$_2$F$_3$), 128.8 (Ar–C$_6$H$_5$), 128.7 (Ar–C$_6$H$_2$F$_3$), 127.8 (Ar–C$_6$H$_5$), 126.6 (Ar–C$_6$H$_5$), 119.1 (Ar–C$_6$H$_2$F$_3$), 29.6 (*C*H$_2$CH$_2$Si), 14.8 (CH$_2$*C*H$_2$Si).

^{19}F{^{1}H} NMR (470 MHz, CDCl$_3$): δ = 132.5 (d, $^2J_{F,F}$ = 19.9 Hz, 6 F), –156.1 (t, $^2J_{F,F}$ = 19.9 Hz, 3 F)

^{29}Si{^{1}H} NMR (99 MHz, CDCl$_3$): δ = 8.2.

MS (EI, 70 eV): *m*/*z* = 525.7 [M – C$_6$H$_5$F]$^+$, 420.8 [M – C$_8$H$_9$]$^+$.

Anal. Calcd (%) for $C_{26}H_{15}F_9Si$: C, 59.32; H, 2.87. Found: C, 59.40; H, 2.92.

Tris(4-fluorophenyl)(phenylethyl)silane (6)

Prepared according to the General Procedure using 1-bromo-4-fluorobenzene (1.4 mL, 13 mmol, 3 equiv), diethyl ether (100 mL), *n*-butyllithium (1.6 M in *n*-hexane, 7.9 mL, 13 mmol, 3 equiv) and trichloro(phenylethyl)silane (1.0 g, 4.3 mmol, 1 equiv). Column chromatography (*n*-pentane) and recrystallization from *n*-hexane afforded **6** as colorless crystals.

Yield: 1.4 g (3.3 mmol, 78%).

AT-IR: 3061, 3026, 2927, 2863, 1907, 1884, 1581, 1496, 1454, 1385, 1224, 1160, 1103, 1012, 896, 820, 765, 724, 699, 687, 644, 595, 560, 517, 451, 424.

^{1}H NMR (500 MHz, C$_6$D$_6$): δ = 7.24 (m, 6 H, Ar$_F$H), 7.19 (m, 2 H, ArH), 7.06 (m, 3 H, ArH), 6.88 (m, 6 H, Ar$_F$H), 2.65 (m, 2 H, CH$_2$*CH*$_2$Si), 1.50 (m, 2 H, *CH*$_2$CH$_2$Si).

^{13}C{^{1}H} NMR (126 MHz, C$_6$D$_6$): δ = 164.6 (Ar–C$_6$H$_4$F), 144.7 (Ar–C$_6$H$_5$), 137.9 (Ar–C$_6$H$_4$F), 130.3 (Ar–C$_6$H$_4$F), 128.8 (Ar–C$_6$H$_5$), 128.1 (Ar–C$_6$H$_5$), 126.3 (Ar–C$_6$H$_5$), 115.6 (Ar–C$_6$H$_4$F), 30.4 (*C*H$_2$CH$_2$Si), 16.1 (CH$_2$*C*H$_2$Si).

^{19}F{^{1}H} NMR (470 MHz, C$_6$D$_6$): δ = 145.7 (s).

^{29}Si{^{1}H} NMR (99 MHz, C$_6$D$_6$): δ = 11.1.

MS (EI, 70 eV): *m*/*z* = 322.1 [M – C$_6$H$_5$F]$^+$, 313.1 [M – C$_8$H$_9$]$^+$.

HRMS: *m*/*z* calcd for $C_{26}H_{21}F_3Si^+$: 418.13591; found: 418.13563.

Anal. Calcd (%) for $C_{26}H_{21}F_3Si$: C, 74.61; H, 5.06. Found: C, 74.90; H, 5.05.

Phenylethyltriphenylsilane (7)

Prepared according to the General Procedure using bromobenzene (1.3 mL, 13 mmol, 3 equiv), diethyl ether (100 mL), *n*-butyllithium (1.6 M in *n*-hexane, 7.9 mL, 13 mmol, 3 equiv) and trichloro(phenylethyl)silane (1.0 g, 4.3 mmol, 1 equiv). Column chromatography (*n*-pentane) and recrystallization from *n*-hexane afforded **7** as colorless crystals.

Yield: 1.4 g (3.9 mmol, 92%).

AT-IR: 3063, 3024, 2995, 2931, 2898, 2878, 1600, 1584, 1487, 1452, 1425, 1384, 1328, 1306, 1259, 1173, 1131, 1107, 1065, 1027, 996, 914, 893, 762, 739, 727, 712, 696, 669, 620, 574, 507, 483, 434, 422 cm^{-1}.

^{1}H NMR (500 MHz, C$_6$D$_6$): δ = 7.59 (m, 6 H, ArH), 7.19 (m, 9 H, ArH), 7.14 (m, 2 H, ArH), 7.05 (m, 6 H, Ar$_F$H), 2.81 (m, 2 H, CH$_2$*CH*$_2$Si), 1.69 (m, 2 H, *CH*$_2$CH$_2$Si).

^{13}C{^{1}H} NMR (126 MHz, C$_6$D$_6$): δ = 145.2 (Ar–C), 136.1 (Ar–C), 135.4 (Ar–C), 129.8 (Ar–C), 128.7 (Ar–C), 128.3 (Ar–C), 128.2 (Ar–C), 126.0 (Ar–C), 30.6 (*C*H$_2$CH$_2$Si), 16.2 (CH$_2$*C*H$_2$Si).

^{29}Si{^{1}H} NMR (99 MHz, C$_6$D$_6$): δ = 10.9.

MS (EI, 70 eV): *m*/*z* = 285.9 [M – C$_8$H$_9$]$^+$, 182.9 [M – C$_{14}$H$_{14}$]$^+$.

Anal. Calcd (%) for $C_{26}H_{24}Si$: C, 85.66; H, 6.64. Found: C, 85.48; H, 6.53.

[(Pentafluorophenyl)ethynyl]triphenylsilane (10)

To a degassed solution of ethynyltriphenylsilane (1.0 g, 3.5 mmol, 1 equiv), diisopropylamine (1.4 mL, 10 mmol, 2 equiv) and bromopentafluorobenzene (0.5 mL, 4 mmol, 1 equiv) in THF (15 mL), a mixture of [Pd(PPh$_3$)$_4$] (100 mg, 0.12 mmol, 3.0 mol%) and CuI (50 mg, 0.30 mmol, 7.5 mol%) was added. The solution was stirred at 60 °C for 4 d and the resulting brown suspension was filtered to give an orange solution. After removing the solvent under reduced pressure, the crude brown solid was purified by filtration through silica gel with *n*-pentane to give a colorless solid. Crystallization from *n*-hexane afforded **10** as colorless crystals.

Yield: 1.4 g (3.1 mmol, 89%).

AT-IR: 3067, 3023, 3003, 2962, 2174, 1647, 1588, 1567, 1517, 1497, 1427, 1372, 1260, 1187, 1112, 1032, 979, 867, 855, 800, 740, 696, 660, 580, 568, 501, 469, 460, 453, 431, 420 cm^{-1}.

^{1}H NMR (500 MHz, C$_6$D$_6$): δ = 7.84 (m, 6 H, ArH), 7.19 (m, 9 H, ArH).

^{13}C{^{1}H} NMR (126 MHz, C$_6$D$_6$): δ = 147.9 (Ar–C$_6$F$_5$), 142.0 (Ar–C$_6$F$_5$), 137.6 (Ar–C$_6$F$_5$), 136.0 (Ar–C$_6$H$_5$), 132.8 (Ar–C$_6$H$_5$), 130.7 (Ar–C$_6$H$_5$), 128.6 (Ar–C$_6$H$_5$), 105.0 (*C*≡C–Si), 99.9 (Ar–C$_6$F$_5$), 92.2 (C≡*C*–Si).

^{19}F{^{1}H} NMR (470 MHz, C$_6$D$_6$): δ = 135.8 (m, 2 F, *o*-F), –152.1 (m, *p*-F), –162.2 (m, 2 F, *m*-F).

^{29}Si{^{1}H} NMR (99 MHz, C$_6$D$_6$): δ = 27.6.

MS (EI, 70 eV): *m*/*z* = 372.6 [M – C$_6$H$_5$]$^+$.

Anal. Calcd (%) for $C_{26}H_{15}F_5Si$: C, 69.32; H, 3.36; F, 21.09; Si, 6.23. Found: C, 69.58; H, 3.67; F, 20.53; Si, 6.11.

[(Pentafluorophenyl)ethyl]triphenylsilane (11)

To a solution of [(pentafluorophenyl)ethynyl]triphenylsilane (100 mg, 0.22 mmol), in MeOH (15 mL), one spatula of Pd(C) (10 wt.% loading) was added. The black suspension was stirred at ambient temperature for 13 h under a continuous flow of hydrogen. After filtration and removing the solvent under reduced pressure, [(pentafluorophenyl)ethyl]triphenylsilane was obtained as colorless crystals.

Yield: 81 mg (0.18 mmol, 81%).

AT-IR: 3030, 3051, 3011, 2929, 1658, 1588, 1519, 1499, 1427, 1321, 1294, 1262, 1216, 1181, 1150, 1111, 995, 977, 891, 821, 773, 742, 696, 667, 505, 487, 477, 459 cm^{-1}.

^{1}H NMR (500 MHz, C6D6): δ = 7.57 (m, 6 H, ArH), 7.19 (m, 9 H, ArH), 2.62 (m, 2 H, CH$_2$*CH*$_2$Si), 1.49 (m, 2 H, *CH*$_2$CH$_2$Si).

^{13}C{^{1}H} NMR (126 MHz, C$_6$D$_6$): δ = 144.9 (Ar–C$_6$F$_5$), 139.6 (Ar–C$_6$F$_5$), 137.6 (Ar–C$_6$F$_5$), 135.9 (Ar–C$_6$H$_5$), 134.5 (Ar–C$_6$H$_5$), 130.1 (Ar–C$_6$H$_5$), 128.5 (Ar–C$_6$H$_5$), 117.9 (Ar–C$_6$F$_5$), 17.5 (*C*H$_2$CH$_2$Si), 14.4 (CH$_2$*C*H$_2$Si).

^{19}F{^{1}H} NMR (470 MHz, C$_6$D$_6$): δ = 145.7 (m, 2 F, *o*-F), –159.2 (m, *p*-F), –163.5 (m, 2 F, *m*-F).

^{29}Si{^{1}H} NMR (99 MHz, C$_6$D$_6$): δ = 11.3.

Anal. Calcd (%) for $C_{26}H_{19}F_5Si$: C, 68.71; H, 4.21; F, 20.90; Si, 6.18. Found: C, 68.45; H, 4.39; F, 21.01; Si, 6.06.

(4-Methylphenethyl)tris(pentafluorophenyl)silane (13)

Prepared according to the General Procedure using 1-bromo-2,3,4,5,6-pentafluorobenzene (1.6 mL, 13 mmol, 3 equiv), diethyl ether (100 mL), *n*-butyllithium (1.6 M in *n*-hexane, 7.9 mL, 13 mmol, 3 equiv) and trichloro(4-methylphenethyl)silane (1.1 g, 4.3 mmol, 1 equiv). Column chromatography (*n*-pentane) and recrystallization from *n*-hexane afforded **13** as colorless crystals.

Yield: 2.2 g (3.4 mmol, 82%).

AT-IR: 2929, 2895, 2874, 1642, 1607, 1582, 1518, 1455, 1398, 1378, 1314, 1286, 1167, 1091, 1030, 964, 907, 856, 838, 819, 802, 778, 759, 720, 693, 671, 629, 619 cm^{-1}.

^1H NMR (500 MHz, C_6D_6): δ = 6.96 (m, 4 H, ArH), 2.65 (m, 2 H, CH_2Si), 2.13 (s, 3 H, $PhCH_3$), 1.91 (t, $J_{H,H}$ = 8.3 Hz, 2 H, CH_2CPh).

$^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6): δ = 149.4 (Ar–C_6F_5), 143.7 (Ar–C_6F_5), 149.3 (Ar–C_6H_4), 137.7 (Ar–C_6F_5), 136.3 (Ar–C_6H_4), 129.6 (Ar–C_6H_4), 128.0 (Ar–C_6H_4), 104.6 (Ar–C_6F_5), 29.3 (Ph–CH_2), 29.9 (Ph–CH_3), 17.3 (Si–CH_2).

$^{19}F\{^1H\}$ NMR (470 MHz, C_6D_6): δ = 126.8 (m, 6 F, *o*-F), –146.6 (m, 3 F, *p*-F), –159.6 (m, 2 F, *m*-F).

$^{29}Si\{^1H\}$ NMR (99 MHz, C_6D_6): δ = 23.7.

Anal. Calcd (%) for $C_{27}H_{11}F_{15}Si$: C, 50.01; H, 1.71. Found: C, 50.27; H, 1.34.

[2-(Naphth-2-yl)ethyl]tris(pentafluorophenyl)silane (15)

Prepared according to the General Procedure using 1-bromo-2,3,4,5,6-pentafluorobenzene (1.0 mL, 8.0 mmol, 3 equiv), diethyl ether (100 mL), *n*-butyllithium (1.6 M in *n*-hexane, 5.0 mL, 8.0 mmol, 3 equiv) and trichloro[2-(naphth-2-yl)ethyl]silane (0.78 g, 2.7 mmol, 1 equiv). Column chromatography (*n*-pentane) and recrystallization from *n*-hexane afforded **15** as colorless crystals.

Yield: 1.4 g (2.1 mmol, 76%).

AT-IR: 3069, 2968, 2933, 2916, 2862, 1644, 1518, 1461, 1404, 1382, 1373, 1289, 1178, 1156, 1142, 1083, 967, 924, 898, 854, 819, 782, 766, 758, 740, 725 cm^{-1}.

^1H NMR (500 MHz, C_6D_6): δ = 7.60 (m, 3 H, ArH), 7.43 (s, 1 H, ArH), 7.26 (m, 2 H, ArH), 7.18 (dd, $J_{H,H}$ = 8.47 Hz, $J_{H,H}$ = 1.83 Hz, 2 H, ArH), 2.83 (m, 2 H, CH_2Si), 2.00 (m, 2 H, CH_2–Naph).

$^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6): δ = 149.4 (Ar–C_6F_5), 143.7 (Ar–C_6F_5), 139.6 (Ar–$C_{10}H_7$), 137.7 (Ar–C_6F_5), 129.0 (Ar–C_6H_5), 134.1 (Ar–$C_{10}H_7$), 132.8 (Ar–$C_{10}H_7$), 128.8 (Ar–$C_{10}H_7$), 128.0 (Ar–$C_{10}H_7$), 126.7 (Ar–$C_{10}H_7$), 126.4 (Ar–$C_{10}H_7$), 126.1 (Ar–$C_{10}H_7$), 104.5 (Ar–C_6F_5), 30.0 (Naph–CH_2), 16.9 (Si–CH_2).

$^{19}F\{^1H\}$ NMR (470 MHz, C_6D_6): δ = 126.8 (m, 2 F, *o*-F), –146.5 (m, *p*-F), –159.6 (m, 2 F, *m*-F).

$^{29}Si\{^1H\}$ NMR (99 MHz, C_6D_6): δ = 23.8.

Anal. Calcd (%) for $C_{30}H_{11}F_{15}Si$: C, 52.64; H, 1.62. Found: C, 52.24; H, 1.60.

(Phenylethyl)tris(2,3,4,5-tetrafluoropyridyl)silane (16)

To a solution of tetrafluoropyridine (2.5 mL, 25 mmol, 3 equiv) in anhydrous diethyl ether (100 mL) at –78 °C, *n*-butyllithium (1.6 M in *n*-hexane, 15.6 mL, 25 mmol, 3 equiv) was added. After 1 h, trichlorophenylethylsilane (2.0 g, 8.3 mmol, 1 equiv) was added dropwise by using a syringe over a period of 5 min. After complete addition, the solution was allowed to slowly warm to ambient temperature and stirred for 12 h. The resulting yellow/brownish suspension was dried in vacuum and suspended in anhydrous *n*-hexane (100 mL). The solid was filtered off and washed with anhydrous diethyl ether (100 mL). The diethyl ether was removed under reduced pressure to give a pale-yellow solid. Recrystallization from anhydrous diethyl ether afforded **16** as colorless crystals.

Yield: 3.8 g (6.5 mmol, 78%).

AT-IR: 3029, 2963, 1639, 1603, 1465, 1440, 1423, 1397, 1380, 1295, 1260, 1231, 1186, 1141, 1097, 1024, 992, 941, 936, 913, 903, 877, 862, 801, 764, 732, 715, 693, 585, 554, 534, 490, 462, 445, 434 cm^{-1}.

^1H NMR (500 MHz, C_6D_6): δ = 7.01 (m, 3 H, ArH), 6.87 (m, 2 H, ArH), 2.50 (m, 2 H, CH_2Si), 1.76 (m, 2 H, CH_2Ph).

$^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6): δ = 144.4 (Ar–C_5NF_4), 144.0 (Ar–C_5NF_4), 141.0 (Ar–C_6H_5), 128.9 (Ar–C_6F_5), 128.0 (Ar–C_6H_5), 127.4 (Ar–C_6H_5), 123.1 (Ar–C_6H_5), 104.6 (Ar–C_6F_5), 29.3 (Ph–CH_2), 29.0 (Ph–CH_3), 14.8 (Si–CH_2).

$^{19}F\{^1H\}$ NMR (470 MHz, C_6D_6): δ = 89.1 (m, 6 F), –128.6 (m, 6 F).

$^{29}Si\{^1H\}$ NMR (99 MHz, C_6D_6): δ = 24.7.

Anal. Calcd (%) for $C_{23}H_9F_{12}N_3Si$: C, 47.53; H, 1.55; N, 7.20. Found: C, 48.34; H, 1.81; N, 7.03.

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0039-1690785.

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