Polyfluorinated Functionalized *m*-Terphenyls. New Substituents and Ligands in Organometallic Synthesis

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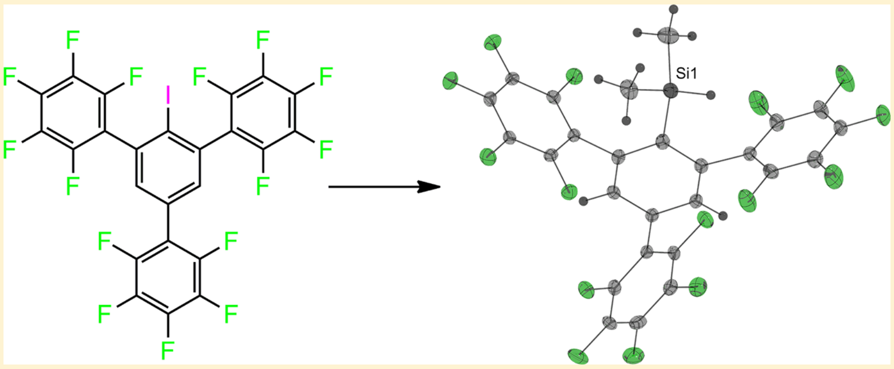
Supporting Information



ABSTRACT: The synthesis and structural characterization of polyfluorinated arenes 2,4,6-$(C_6F_5)_3C_6H_2X$ and 2,6-$(C_6F_5)_2$-4-BrC_6H_2X (X = NO_2, Cl, Br) obtained in the Ullmann-type cross coupling reaction is reported. The nitro derivatives were reduced to the aromatic amines. The α-diimine $[2,4,6\text{-}(C_6F_5)_3C_6H_2NCMe]_2$ and 2,4,6-$(C_6F_5)_3C_6H_2I$ were obtained in condensation and Sandmeyer reactions, respectively, from the corresponding amine. The syntheses of 2,4,6-$(C_6F_5)_3C_6H_2NHC$-(O)H, 2,4,6-$(C_6F_5)_3C_6H_2NC$, and 2,4,6-$(C_6F_5)_3C_6H_2Si(X)Me_2$ (X = H, F, Cl) are also described.

Bulky aryl groups are widely used to kinetically stabilize compounds with remarkable structures,[1,2] and they offer the possibility to explore the reactivity of rare species.[3−6] Large bulky groups also provide thermodynamic stability to the unsaturated monomers, with respect to oligomers.[7,8] However, some bulky groups, e.g. the supermesityl group, have an adverse effect on the stability as steric pressure gives rise to repulsion and formation of byproducts.[9,10]

Among the most common and widely used *m*-terphenyls are those of type 2,6-$Ar_2C_6H_3X$ (Ar = aryl group, X = functional group),[11] in contrast to those of type 3,5-$Ar_2C_6H_3X$.[12] The synthesis of both type *m*-terphenyl precursors is based on the procedure developed by Hart.[13,14] Later on Power et al. proposed further improvements to the originally used 2,6-$Ar_2C_6H_3X$.[11] Siegel et al. synthesized and used for the stabilization of silylium ions the first *m*-terphenyls containing fluorine atoms.[15,16] Wehmschulte et al. have reported thermally *m*-terphenyl stabilized cationic aluminum species.[17,18] A rich and interesting coordination chemistry using sterically encumbering isocyanide ligands has also been developed.[19−22] Recently Schrock et al. investigated the catalytic properties of some 2,6-bis(pentafluorophenyl)phenoxide complexes of molybdenum and reported a different behavior compared to complexes containing phenolates of the type 2,6-$Ar_2C_6H_3O^-$ (Ar = 2,4,6-$Me_3C_6H_2$ or 2,4,6-$iPr_3C_6H_2$). The different catalytic properties of the molybdenum complexes were attributed to the electron-deficient character of the polyfluorinated terphenolates in combination with their steric bulk.[23,24] Isocyanide derivatives with an electron withdrawing *m*-terphenyl backbone were recently used as ligands in molybdenum coordination chemistry.[25]

Aromatic C−C bond formation with an aromatic group containing fluorine atoms has been done in Suzuki cross-coupling reactions,[26−28] by direct arylation reactions (C−H functionalization) between aryl halides and electron-deficient fluorinated benzenes,[29,30] and in Ullmann-type cross-coupling reactions.[31−33] The related 2,6-$(2',6'\text{-}F_2C_6H_3)_2C_6H_3I$ was prepared by a Negishi coupling of a 2,6-dibromosubstituted triazene with the corresponding organozinc halide.[15]

We envisaged the design of novel substituents with a *m*-terphenyl backbone which contain electron-deficient pentafluorophenyl groups in flanking positions. *m*-Terphenyl substituents with electron withdrawing flanking groups are less commonly used in coordination and organometallic chemistry. We hence became interested in studying the advantages and limitations of these substituents in comparison with the classical *m*-terphenyl ligands.

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Theoretical studies have shown that the electron deficient arenes can stabilize both cations and especially anions.[34−36] In theory, novel types of compounds could be stabilized using these ligands, through intramolecular interactions between the electron-deficient groups and a metal center located in their common *ortho* position due to the fact that C_6F_5 groups have both dipole and quadrupole moments. Moreover, the C_6F_5 groups could also stabilize a heteroatom located in their common *ortho* position by F → M intramolecular coordination, as previously reported for the related ligand 2,6-(2′,6′-$F_2C_6H_3)_2C_6H_3$.[15,16]

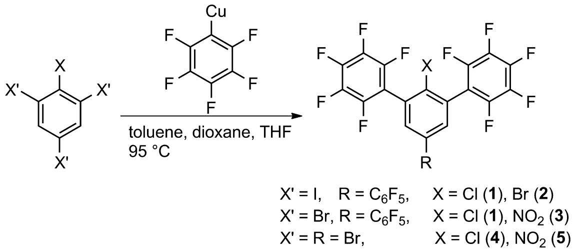
We report here a series of polyfluorinated arenes with *m*-terphenyl backbone 2,4,6-$(C_6F_5)_3C_6H_2X$ [X = Cl (**1**), Br (**2**), NO_2 (**3**)] and 2,6-$(C_6F_5)_2$-4-BrC_6H_2X [X = Cl (**4**), NO_2 (**5**)]. Reduction of **3** and **5** affords 2,4,6-$(C_6F_5)_3C_6H_2NH_2$ (**6**) and 2,6-$(C_6F_5)_2$-4-Br-$C_6H_2NH_2$ (**7**), respectively. Also we present functional group transformations that allowed the synthesis of 2,4,6-$(C_6F_5)_3C_6H_2I$ (**8**), [2,4,6-$(C_6F_5)_3C_6H_2NCMe]_2$ (**9**), and 2,4,6-$(C_6F_5)_3C_6H_2NHC(O)H$ (**10**). Isocyanide 2,4,6-$(C_6F_5)_3C_6H_2NC$ (**11**) can be obtained almost quantitatively starting from **10**. The symmetrical derivative 1,3,5-$(C_6F_5)_3C_6H_3$ (**12**) is obtained in better yields than previously reported,[37] using **6** as starting material. Metalation with *n*BuLi of **2** or **8** and subsequent reaction with $Me_2Si(H)Cl$ and Me_2SiCl_2, respectively, afford 2,4,6-$(C_6F_5)_3C_6H_2Si(H)Me_2$ (**13**) and 2,4,6-$(C_6F_5)_3C_6H_2Si(Cl)Me_2$ (**14**). Reaction of **14** with $TlPF_6$ yields 2,4,6-$(C_6F_5)_3C_6H_2Si(F)Me_2$ (**15**). Improved synthesis methods for known starting materials 1,3,5-$Br_3C_6H_2X$ [X = Cl (**16**), NO_2 (**17**)] and 1,3,5-$I_3C_6H_2X$ [X = NH_2 (**18**), Cl (**19**), Br (**20**)] are also provided.

Compounds **1**−**20** were characterized by multinuclear NMR spectroscopy and HRMS. The molecular structures of **3**−**5**, **9**, **13**, and **17** were determined by single-crystal X-ray diffraction. Although the structure of **17** was previously reported,[38] the crystallographic data are not included in CSD. The reduced cell of **17** is different from that previously reported.

■ RESULTS AND DISCUSSION

Synthesis. The compounds 2,4,6-$(C_6F_5)_3C_6H_2X$ [X = Cl (**1**), NO_2 (**3**)] were synthesized by the reaction of 6 equiv of pentafluorophenylcopper with **16** or **17**, respectively, in a mixture of toluene, dioxane, and THF at 95 °C (Scheme 1).[39] 2,4,6-$(C_6F_5)_3C_6H_2X$ [X = Cl (**1**), Br (**2**)] can also be prepared using **19** or **20** as starting materials.

Scheme 1. Synthesis of the Polyfluorinated Arenes 1−5



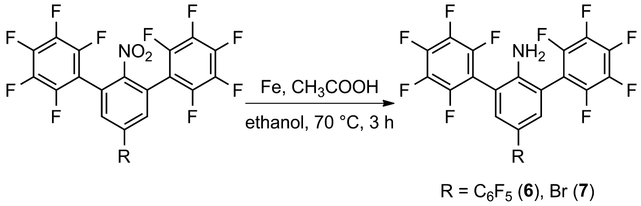
The chloride **1** was obtained in a modest yield (26%) when **16** was used as starting material. Using **19** instead, under the same reaction conditions, the yield of **1** was increased to 92%. Reaction of **20** with C_6F_5Cu proceeded selectively to afford **2** in high yields (84−88%). Attempts to obtain directly the iodide 2,4,6-$(C_6F_5)_3C_6H_2I$ (**8**) by using 1,2,3,5-$I_4C_6H_2$ as starting material were unsatisfactory. In this case the reaction does not proceed selectively and **8** is obtained together with other coupling products. We also attempted to prepare alternatively 2,6-$(C_6F_5)_2C_6H_3I$ by a route adapted from the Hart procedure. In our hands, this method failed to give the desired product.

The compounds 2,6-$(C_6F_5)_2$-4-BrC_6H_2X [X = Cl (**4**), NO_2 (**5**)] were synthesized using 2.6 and 3.6 equiv of C_6F_5Cu and **16** and **17**, respectively. These *m*-terphenyl derivatives, with a design similar to that of the bulky groups used by Schrock,[12] are of particular importance because the bromine can be substituted with a different organic fragment or can be replaced by another functional group. Despite the prolonged reaction time (11 h), the isolated yield of **4** was low (39%). In the same reaction, **1** was also isolated in 10% yield as a side-product. The derivative **5** was obtained after 4 h of reflux in a good yield (77%).

In all the reactions carried out to prepare **4** and **5**, only the coupling products in positions 2 and 6, with respect to the functional group (NO_2 or Cl), were obtained, suggesting that the reactions take place regioselectively. Apparently the substitution of the bromine atoms from position 2 and 6 takes place more readily than the substitution of bromine from position 4.

Reduction of **3** and **5** with Fe^0 and acetic acid (Scheme 2), in ethanol, afforded the corresponding aniline derivatives 2,4,6-$(C_6F_5)_3C_6H_2NH_2$ (**6**) and 2,6-$(C_6F_5)_2$-4-$BrC_6H_2NH_2$ (**7**), respectively, in very good yields.

Scheme 2. Synthesis of 6 and 7



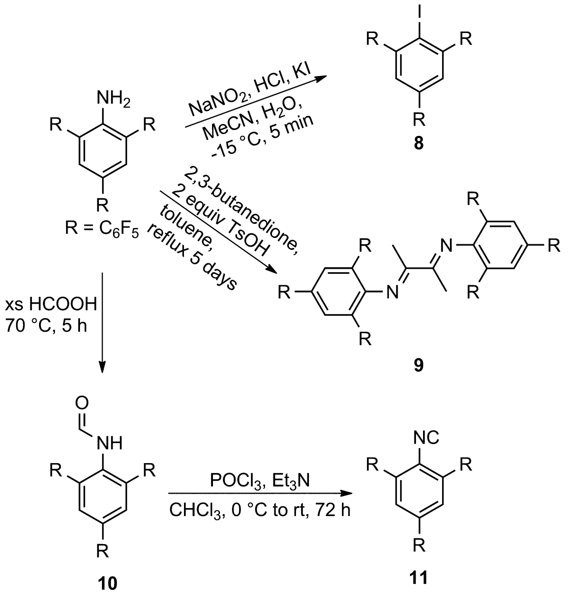
Iodide **8**, for which a direct method of synthesis could not be developed, was obtained by diazotation of the aniline derivative **6** (Scheme 3). By using the previously reported methods for the diazotation of weakly basic amines,[40] only the symmetrical hydrocarbon 1,3,5-$(C_6F_5)_3C_6H_3$ (**12**) was isolated in 80% yield. The synthesis with low yields (less than 3%) of **12** was previously reported.[37] The ^{19}F NMR data of **12** are now available.

By using a modified procedure of Krasnokutskaya et al.,[41] compound **8** was obtained in 85% yield. The aniline derivative **6** was diazotized at −15 °C in less than 5 min in the presence of HCl and $NaNO_2$ in acetonitrile. Subsequent reaction of the diazonium salt with KI afforded **8**. Longer reaction time or higher temperature led to formation of **12** as side product.

The *α*-diimine [2,4,6-$(C_6F_5)_3C_6H_2NCMe]_2$ (**9**) was obtained in the reaction of amine **6** with 2,3-butandione in the presence of 2 equiv of *p*-toluenesulfonic acid and 4 Å molecular sieves in a poor yield (8%) after approximately 5 days of heating the reaction mixture at 130 °C.

Formamide **10** was obtained in 78−83% yields by heating **6** in formic acid for 5 h. The product begins to precipitate after approximately 3 h. Although in the NMR spectra resonances for both isomers of **10** are present (*vide infra*), in the IR spectra only one set of bands was observed. The CO stretching vibration (1705 cm^{-1}) of **10** has a value similar to that of 2,6-

Scheme 3. Synthesis of 8−11



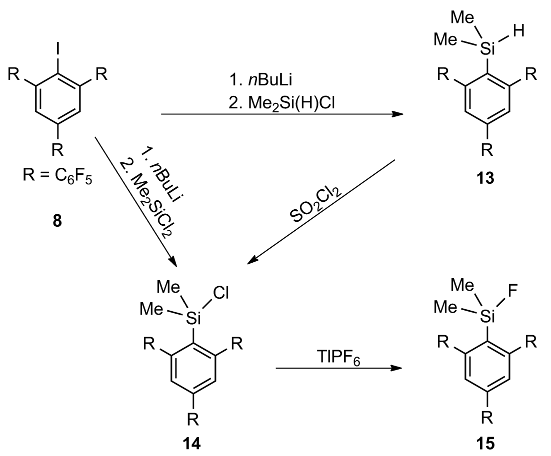
$(3',5'\text{-}(CF_3)_2C_6H_3)_2C_6H_3NHC(O)H$ (1707 cm^{-1})[25] or 2,6-$(2',6'\text{-}i\text{Pr}_2C_6H_3)_2C_6H_3NHC(O)H$ (1699 cm^{-1}),[42] but different from that of 2,6-$\text{Mes}_2C_6H_3NHC(O)H$ (1682 cm^{-1}).[43]

Dehydration of **10** with $POCl_3$ in the presence of triethylamine proceeded readily to afford the isocyanide **11** almost quantitatively. The NC stretching vibration of **11** is 2121 cm^{-1} and is comparable with those of 2,6-$(3',5'\text{-}(CF_3)_2C_6H_3)_2C_6H_3NC$ (2119 cm^{-1}),[25] 2,6-$(2',6'\text{-}i\text{Pr}_2C_6H_3)_2$-$C_6H_3NC$ (2124 cm^{-1}),[42] or 2,6-$\text{Mes}_2C_6H_3NC$ (2120 cm^{-1}).[43]

Metalation in hexane with *n*BuLi of **2** at rt or of **8** at −78 °C affords 2,4,6-$(C_6F_5)_3C_6H_2Li$. The use of THF as solvent in the metalation reaction of **8** is not suitable due to nucleophilic attack of the more reactive *n*BuLi at the F_5C_6 groups.

The reaction of $Me_2Si(H)Cl$ or Me_2SiCl_2 with the *in situ* formed 2,4,6-$(C_6F_5)_3C_6H_2Li$ gives 2,4,6-$(C_6F_5)_3C_6H_2Si(H)Me_2$ (**13**) and 2,4,6-$(C_6F_5)_3C_6H_2Si(Cl)Me_2$ (**14**), respectively (Scheme 4). Alternatively **14** can be obtained by reacting **13** with SO_2Cl_2 in dry CH_2Cl_2 for 18 h. As it does not require any additional purification of the moisture sensitive derivative **14**, the latter synthetic approach is recommended.

Scheme 4. Synthesis of Silanes 13−15



In order to investigate the reactivity of **13** and the behavior of the 2,4,6-$(C_6F_5)_3C_6H_2$ substituent, the synthesis of a silylium ion, similar to those reported by Siegel,[44] was attempted. Reactions of **13** with $[Ph_3C][B(C_6F_5)_4]$ in C_6D_6 did not lead to the formation of the expected product, neither at rt or high temperature. In order to understand the low reactivity of **13** toward $[Ph_3C][B(C_6F_5)_4]$, DFT calculations were carried out (*vide infra*).

In light of the lack of reactivity of **13**, the preparation of the related silylium ion $[2,4,6\text{-}(C_6F_5)_3C_6H_2SiMe_2][PF_6]$ by using **14** as starting material was attempted. However, the reactions of **14** with $TlPF_6$ in acetonitrile at rt afforded only 2,4,6-$(C_6F_5)_3C_6H_2Si(F)Me_2$ (**15**) in almost quantitative yield. This reaction suggests that the silylilum ion had formed *in situ* but abstracted a fluorine atom from the $[PF_6]^-$ anion with formation of **15** and PF_5.

NMR Studies. The ^{19}F NMR spectra of compounds **1**−**3**, **6**, **8**, **10**, **11**, and **13**−**15** exhibit two sets of resonance signals corresponding to *ortho*, *para*, and *meta* fluorine atoms of the two nonequivalent pentafluorophenyl rings located in positions *ortho* and *para* with respect to the functional group.

The ^{13}C NMR spectra of these compounds show the expected singlet resonances corresponding to the carbon atoms of the central aromatic rings. Also the two signals (triplets or triplets of doublets) given by the *ipso* carbon atoms of the two nonequivalent F_5C_6 groups are easily distinguished.

The ^{19}F NMR spectra of compounds **4** and **5** exhibit one set of resonance signals corresponding to the *ortho*, *para*, and *meta* fluorine atoms of the equivalent F_5C_6 groups. Accordingly, only one signal corresponding to the *ipso* carbon atoms of the pentafluorophenyl rings was observed in the ^{13}C NMR spectra for these compounds. The signals corresponding to the carbon atoms directly bonded to fluorine show as distinct doublets of multiplets with $^{1}J_{C-F}$ coupling constants around 250 Hz.

While the ^{1}H NMR spectra of $[2,4,6\text{-}(C_6F_5)_3C_6H_2NCMe]_2$ (**9**) exhibit only one set of resonances for both methyl and aromatic protons, the ^{19}F NMR spectra exhibit two sets of resonances for the *ortho* and *meta* fluorine atoms and one set for the *para* fluorine atoms of the C_6F_5 groups in positions 2 and 6. Although in the ^{13}C NMR spectra the nonequivalence of the carbon atoms bonded to fluorine is not clear due to broad resonances caused by C−F couplings, only one set of signals were observed for the C_{ipso} atoms of the C_6F_5 groups in positions 2 and 6, and one set for the C_6F_5 groups in positions 4. This pattern suggests that the rotation of C_6F_5 groups is restricted around an axis containing a fluorine atom in the *para* position and C_{ipso}.

In the ^{1}H and ^{19}F NMR in $(CD_3)_2CO$, C_6D_6, and $CDCl_3$, both *Z* and *E* isomers of **10** were observed. The molar ratios of the isomers, calculated based on the integrals of the corresponding resonances in ^{1}H NMR spectra, are 1:0.13 in $(CD_3)_2CO$, 1:0.21 in C_6D_6, and 1:0.56 in $CDCl_3$. The assignment of the resonance signals for the *Z* and *E* isomers in the ^{1}H NMR spectra of **10** was based on COSY, ROESY, and HSQC experiments. The ratio of the integral values observed for the two isomers in the ^{1}H NMR was also found in the ^{19}F NMR spectra.

In variable temperature ^{1}H and ^{19}F NMR spectra of **10** in $(CD_3)_2CO$ up to 46 °C or in C_6D_6 up to 70 °C, the coalescence was not reached. This suggests that the amide bond rotation energy barrier of **10** is larger than that in less hindered similar molecules such as *N*-phenylformamide.[45] Indeed, the rotation energy barrier in the gas phase calculated for 2,6-

$(C_6F_5)_2C_6H_3NHC(O)H$, a simplified model for **10**, at the DFT level is 83 kJ/mol. In the same model, at the specified theory level, the energy of the *Z* isomer is 3 kJ/mol smaller than that of the *E* isomer.

In the ^1H NMR spectrum of **13** the chemical shift corresponding to the silicon bonded hydrogen atom is comparable to those observed for previously reported *m*-terphenyl substituted silanes.[15,16,44] The resonance signals for the aromatic and methyl protons of **14** and **15** are slightly downfield shifted compared to the corresponding signal of **13**. In the ^{29}Si NMR spectrum of **13**, the chemical shift of silicon (−19.1 ppm) is also similar to those of other *m*-terphenyl substituted silanes.[15,16,44] The ^{29}Si NMR spectra of **14** and **15** exhibit resonance signals similar to those reported for $PhSi(Cl)Me_2$[46] or 9-(chlorodimethylsilyl)anthracene.[47]

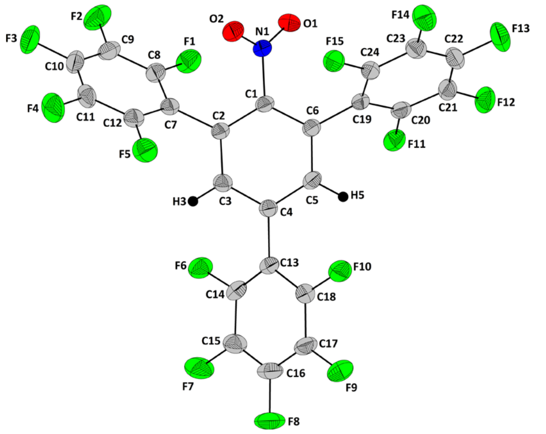


Figure 1. Thermal ellipsoid representation (25% probability) of the molecular structure of **3**.

Molecular Structures of 3–5, 9, and 13. In the molecular structure of **3** (Figure 1), the pentafluorophenyl groups are twisted with respect to the central aromatic ring due to intramolecular C–H···F bonds being established between the hydrogen atoms of the central aryl group and a fluorine atom of the C_6F_5 groups in positions 2 and 6 with respect to the NO_2 group, and both fluorine atoms of the C_6F_5 in position 4. This leads to a propeller-like arrangement with angles between the planes containing the C_6F_5 groups and the plane of the central benzene ring of 60.6(1), 51.9(2), and 36.1(1)°. The angle between the plane containing the NO_2 group and the plane of the central benzene ring is 47.2(3)°.

In the crystal, the molecules of **3** are interconnected through C–F···π interactions (see Supporting Information).

In the molecular structures of **4** (Figure 2) and **5** (Figure 3), the angles between the planes containing the C_6F_5 groups and the central benzene ring are larger than those in **3** [**4**: 65.9(1), 73.7(1)°; **5**: 63.2(1), 78.7(2)°]. In **5** the plane containing the NO_2 group is rotated with 44.9(3)° with respect to the plane of the central benzene ring, similar to the value found in **3**. In the crystals of **4** and **5**, there are a plethora of C–X···π (X = halogen) intermolecular interactions which lead to supramolecular assemblies (see Supporting Information).

In the crystal, molecules of **9** are centrosymmetric with respect to an inversion center located at half the distance between the carbon atoms of the imino groups (Figure 4). The C_6F_5 groups in positions 2 and 6 form a wedge shape cavity in which the methyl and imino groups are located.

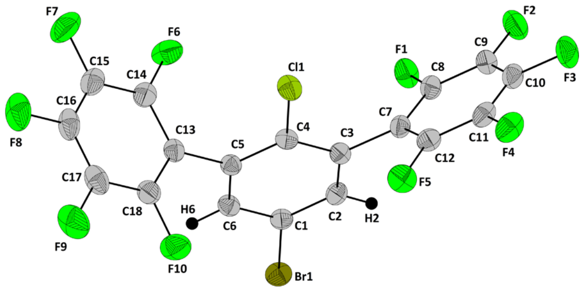


Figure 2. Thermal ellipsoid representation (25% probability) of the molecular structure of **4**.

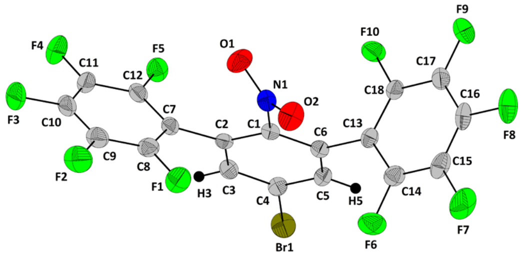


Figure 3. Thermal ellipsoid representation (25% probability) of the molecular structure of **5**.

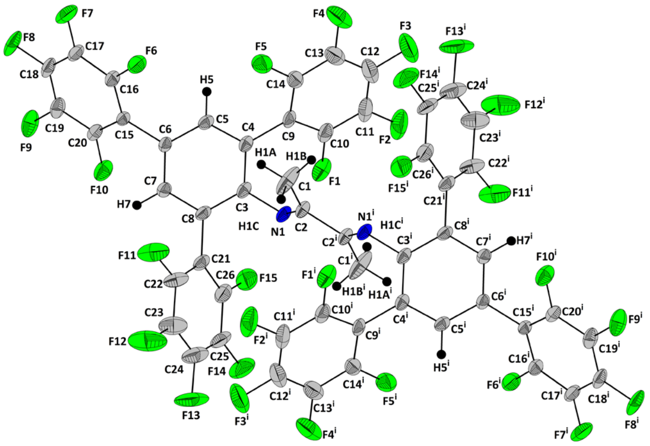


Figure 4. Thermal ellipsoid representation (25% probability) of the molecular structure of **9**.

Intermolecular C–H···F contacts are observed between the one hydrogen atom of the methyl groups and a fluorine atom (see Supporting Information).

The molecular structure of **13** is depicted in Figure 5. The $Si-C_{aryl}$ bond length [1.906(6) Å] is in the range of those found in $2,6\text{-}(2',4',6'\text{-}i\mathrm{Pr}_3C_6H_2)_2C_6H_3Si(H)F_2$ [1.990(2) Å][48] or $2,6\text{-}(2',4',6'\text{-}i\mathrm{Pr}_3C_6H_2)_2C_6H_3Si(H)R$ (R = 9,10-dihydroanthracendi-9,10-yl) [1.8908(17), 1.8946(16) Å],[49] $2,6\text{-}(2',4',6'\text{-}i\mathrm{Pr}_3C_6H_2)_2C_6H_3Si(H)R$ (R = 9,10-dihydroanthracen-9-yl) [1.8890(19) Å],[49] or $2,6\text{-}Mes_2C_6H_3Si(H)Ph_2$ [1.9043(18) Å].[49] The angles between the planes containing the central benzene ring and the flanking C_6F_5 are 88.0(2) and 85.5(2)°. The C_6F_5 group in the position *para* to silicon is rotated by 45.4(2)° with respect to the central benzene ring. Also in the crystals of **13** there are intermolecular C–F···π and C–H···π interactions which lead to supramolecular assemblies. The representation of these interactions as well as interatomic distances and angles is included in the Supporting Information.

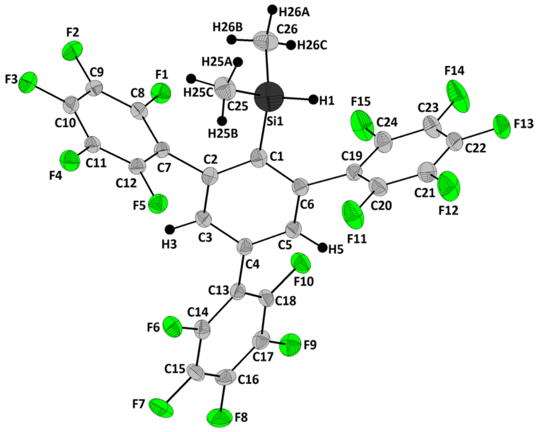


Figure 5. Thermal ellipsoid representation (30% probability) of the molecular structure of **13**.

Theoretical Studies. Theoretical calculations at the DFT level were carried out on **13** as well as on the related 2,6-(2′,6′-$F_2C_6H_3)_2C_6H_3Si(H)Me_2$ and 2,6-(2′,6′-$Me_2C_6H_3)_2C_6H_3Si(H)$-Me_2. The last two compounds were successfully used as starting materials for compounds containing silylium ions.[15,44]

The comparison of the calculated and determined bond lengths and bonding angles for **13** is presented in Supporting Information, Table 15. The Si−C bond lengths and C−Si−C and C−Si−H bond angles are within 3% agreement to those determined from the crystallographic data. In the calculated structure the pentafluorophenyl groups are oriented slightly differently with respect to the central benzene ring. The Wiberg bond indices for Si−H in the calculated structures have similar values for 2,6-(2′,6′-$F_2C_6H_3)_2C_6H_3Si(H)Me_2$ (0.9217) and for **13** (0.9211) and are slightly larger than those for 2,6-(2′,6′-$Me_2C_6H_3)_2C_6H_3Si(H)Me_2$ (0.9178). The calculated bond indices suggest that in **13** the Si−H bond is stronger than that in the previously reported silanes. These values are also consistent with the IR data.

The energies of the reactions between 2,6-(2′,6′-$F_2C_6H_3)_2C_6H_3Si(H)Me_2$, 2,6-(2′,6′-$Me_2C_6H_3)_2C_6H_3Si(H)$-$Me_2$, **13**, and $[Ph_3C]^+$ with formation of the corresponding silylium ions and Ph_3CH are −37.89, −25.29, and 14.82 kJ·mol^{-1}, respectively. These values indicate that, at the employed theory level, the reaction between the trityl cation and **13** is not energetically favorable.

■ CONCLUSIONS

In conclusion, we report a simple synthetic method for polyfluorinated functionalized *m*-terphenyls that may be useful ligands and substituents in novel organometallic compounds with sterically demanding electron withdrawing substituents. Further studies on the use of these *m*-terphenyls in the main group organometallic chemistry are in progress.

■ EXPERIMENTAL SECTION

General Considerations. Unless otherwise indicated, starting materials were used without further purification. The solvents were distilled, under argon atmosphere, from appropriate drying agents (sodium for dioxane, hexane, and toluene, potassium for tetrahydrofuran, phosphorus oxide for dichloromethane, calcium hydride for acetonitrile) prior to use. All the other solvents were used as received. The preparations of compounds **1**−**5**, **9**, **11**, and **13**−**15** were performed under an argon atmosphere, and the work up of the reactions was carried out in air except for **14**. For the column and thin layer chromatography was used 0.060−0.200 mm, 60 Å silica gel, and silica gel 60 coated aluminum sheets with F_{254} indicator, respectively.

The NMR spectra were recorded on Bruker Avance III DPX-360, Bruker Avance III 400, and Bruker Avance III 600 spectrometers. ^1H and ^{13}C chemical shifts are reported in δ units (ppm) relative to the residual peak of solvent ($CHCl_3$, 7.26 ppm; $CD_3C(O)CD_2H$ 2.05 ppm; C_6D_5H 7.16 ppm) in the ^1H NMR spectra and to the peak of the deuterated solvent ($CDCl_3$ 77.16 ppm; $(CD_3)_2CO$ 29.84 ppm; C_6D_6 128.06 ppm) in ^{13}C NMR spectra.[50] ^{19}F and ^{29}Si NMR spectra are reported in δ units (ppm) relative to $CFCl_3$ (0 ppm) and Me_4Si (0 ppm), respectively, using the chemical shift of the lock solvent as a reference. The ^{13}C, ^{19}F, and ^{29}Si reported spectra are ^1H decoupled. The chemical shifts in the ^{13}C NMR spectra of the compounds substituted with pentafluorophenyl groups in positions 2, 4, and 6 are given only as ranges for the observed multiplets, without taking into account the $^1J_{C-F}$ coupling constants.

HRMS APCI(+) spectra were recorded on a Thermo Scientific Orbitrap XL spectrometer. Data analysis and calculations of the theoretical isotopic patterns were carried out with the Xcalibur software package.[51]

X-ray Crystallography. Crystallographic data were collected at rt on a Bruker Smart APEX II (**3**−**5**, **9**, **17**) or at 173 K on a STOE IPDS (**13**) diffractometer with graphite monocromators using Mo Kα radiation (0.71073 Å). Crystals were mounted on a loop using Paraton or Kel-F (**13**) oil. The structures were solved and refined with the SHELXL-97 or SHELX-2013 software package.[52] All the non-hydrogen atoms were treated anisotropically. Hydrogen atoms were included in riding positions with the isotropic thermal parameters set 1.2 times the thermal parameters of the carbon atoms directly attached for the aromatic hydrogen atoms and 1.5 times for the hydrogen atoms of the methyl groups. The hydrogen atom bonded to silicon in **13** was located in the electron density map and its position and isotropic temperature factor refined. The ring centroids and intramolecular and intermolecular interactions were calculated using PLATON.[53] The representation of the crystallographic data and calculations of the angles between the planes were carried out using Diamond.[54]

Theoretical Calculations. Theoretical calculations at the DFT level on 2,6-$(C_6F_5)_2C_6H_3NHC(O)H$, a slightly smaller model for compound **10**, were carried out using ORCA 2.9.1 whereas ORCA 3.0.0 and 3.0.1 were used for 2,6-(2′,6′-$F_2C_6H_3)_2C_6H_3Si(H)Me_2$ and 2,6-(2′,6′-$Me_2C_6H_3)_2C_6H_3Si(H)Me_2$ **13** and the silylium ions.[55] The calculations were carried out using the BP86 functional and atom-pairwise dispersion correction with the zero-damping scheme.[56−58] The def2-TVP basis set was used for all the atoms of **10**,[59,60] and def2-SVP for all the atoms of **13**, 2,6-(2′,6′-$F_2C_6H_3)_2C_6H_3Si(H)Me_2$, 2,6-(2′,6′-$Me_2C_6H_3)_2C_6H_3Si(H)Me_2$, and the corresponding silylium ions. The energy minimum for the calculated structures was confirmed by the frequencies calculation. Wiberg bond indices were calculated with NBO 5.9.[61] The DFT calculated molecular structures were represented using Chemcraft, whereas the electrostatic potential maps were represented using PyMOL 1.7.0.1.[62]

Synthesis of 2,4,6-$(C_6F_5)_3C_6H_2Cl$ (1). A 100 mL, three-necked, round-bottom flask fitted with a reflux condenser, argon inlet, and dropping funnel was charged with magnesium turnings (0.68 g, 27.94 mmol). Anhydrous THF (50 mL) was collected in the dropping funnel. After THF (20 mL) was introduced into the flask, C_6F_5Br (5.75 g, 23.3 mmol) was added in the dropping funnel. *Via* syringe, 1,2-$Br_2C_2H_4$ (0.875 g, 4.66 mmol) was introduced in the flask and the mixture was heated gently to reflux. Continuing to heat the reaction mixture, the solution of C_6F_5Br in THF was added dropwise from the dropping funnel at a rate that afforded a gentle reflux. The reaction mixture was stirred at 86 °C (oil bath temperature) for 1.5 h and then was allowed to cool to rt. The resulting dark brown solution containing the C_6F_5MgBr was added over anhydrous copper(I) bromide (5.01 g 34.9 mmol), under argon atmosphere, in a 250 mL three-necked, round-bottom flask fitted with a reflux condenser, argon inlet, and dropping funnel. The brown suspension was stirred at rt for 30 min, dioxane (7 mL) was added to the reaction mixture, and the resulting gray suspension was stirred at rt for another 30 min. To this suspension was added a solution of **19** (1.900 g, 3.88 mmol) in 50 mL of toluene. The mixture was stirred at 95 °C (oil bath temperature) for approximately 18 h over 3 days. The reaction mixture was filtered through a pad of silica gel approximately 6 cm thick. The solvents were removed from the filtrate using a rotary evaporator. The residue was heated at 65−75 °C (2×10^{-2} mbar) in a sublimation apparatus to remove decafluorobiphenyl. The remaining residue was dissolved in petroleum ether (150 mL) and the solution filtered through a 6 cm thick pad of silica gel. The silica gel pad was further washed with 150 mL of petroleum ether. Evaporation of the solvent gave **1** (2.19 g (92%)) as a white solid. Mp 168−170 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.57 (s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 146.23−145.74 (m), 143.85−143.37 (m), 142.87−142.47 (m), 140.46−139.30 (m), 136.78−136.17 (m), 136.11 (s), 134.96 (s), 128.11 (s), 126.01 (s), 113.06 (td, *J* = 16, 4 Hz), 112.42 (td, *J* = 19, 4 Hz); ^{19}F NMR ($CDCl_3$, 282 MHz): δ −138.88 to −139.09 (m, 4F), −142.58 to −142.78 (m, 2F), −152.14 (tt, *J* = 21 Hz, 2F), −152.48 (t, *J* = 21.0 Hz, 1F), −160.56 to −160.81 (m, 2F), −160.85 to −161.11 (m, 4F); HRMS-APCI (*m*/*z*): $[M]^+$ calcd for $C_{24}H_2ClF_{15}$, 609.96000; found, 609.95886.

Synthesis of 2,4,6-(C_6F_5)$_3$$C_6H_2$Br (2). To a solution of C_6F_5MgBr in THF (100 mL), prepared as described for the synthesis of **1** from magnesium turnings (2.19 g, 90 mmol), was added 1,2-$Br_2C_2H_4$ (2.82 g, 15 mmol) and C_6F_5Br (18.5 g, 75 mmol) over anhydrous copper(I) bromide (13.1 g, 91 mmol), placed, under argon atmosphere, in a 500 mL three-necked, round-bottom flask fitted with a reflux condenser, argon inlet, and dropping funnel. The brown suspension was stirred at rt for 30 min; afterward, dioxane (30 mL) was added over the reaction mixture and the resulting gray suspension was stirred at rt for another 30 min. To this suspension was added a solution of **20** (6.668 g, 12.5 mmol) in toluene (100 mL). The reaction mixture was stirred at 95 °C (oil bath temperature) for approximately 16 h over 3 days. The reaction mixture was filtered through a pad of silica gel approximately 6 cm thick. The solvents were removed from the filtrate using a rotary evaporator affording a slightly oily solid. This product was heated at 75−105 °C (2×10^{-2} mbar) in a sublimation apparatus to remove decafluorobiphenyl and other impurities. The remaining residue (8.1 g) was dissolved in 500 mL of heptane and filtered through a pad of silica gel approximately 6 cm thick. The solvent was recovered and reused to wash again the silica gel pad. **2** (7.22 g, 88%) was obtained as a white solid which contained approximately 3% mol (calculated based on NMR integral ratio) of **12**. Mp 170−172 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.53 (s, 2H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 145.73−145.25 (m), 143.44−142.44 (m), 140.89−140.43 (m), 140.36−139.79 (m), 139.76−138.91 (m), 137.25−136.41 (m), 134.65 (s), 130.65 (s), 127.90 (s), 126.76 (s), 114.43 (td, *J* = 19, 4 Hz), 113.11 (td, *J* = 16, 4 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz): δ −138.87 − −139.05 (m, 4F), −142.56 − −142.71 (m, 2F), −152.29 (t, *J* = 21 Hz, 2F), −152.46 (t, *J* = 21 Hz, 1F), −160.60 − −160.82 (m, 2F), −160.90 − −161.11 (m, 4F); HRMS-APCI (*m*/*z*): $[M]^+$ calcd for $C_{24}H_2BrF_{15}$, 653.90949; found, 653.90750.

Synthesis of 2,4,6-(C_6F_5)$_3$$C_6H_2NO_2$ (3). A solution of C_6F_5MgBr in THF (100 mL), prepared as described for the synthesis of **1** from magnesium turnings (1.75 g, 72 mmol), was added 1,2-$Br_2C_2H_4$ (2.25 g, 12 mmol) and C_6F_5Br (14.8 g, 60 mmol) over anhydrous copper(I) bromide (12.9 g, 90 mmol), placed, under argon atmosphere, in a 500 mL three-necked, round-bottom flask fitted with a reflux condenser, argon inlet, and dropping funnel. The brown suspension was stirred at rt for 30 min; afterward, dioxane (20 mL) was added over the reaction mixture and the resulting gray suspension was stirred at rt for another 30 min. To this suspension was added a solution of **17** (3.600 g, 10 mmol) in toluene (100 mL). The reaction mixture was stirred at 95 °C (oil bath temperature) for approximately 36 h over 4 days. The reaction mixture was filtered through a pad of silica gel approximately 6 cm thick. The solvents were removed from the filtrate using a rotary evaporator affording a slightly oily solid. This product was heated at 85−95 °C (2×10^{-2} mbar) in a sublimation apparatus to remove decafluorobiphenyl. The remaining residue was washed with pentane (4×10 mL) and decanted, and the solid was dried at reduced pressure to give **3** (3.93 g, 63%) as a tan solid. Mp 185−187 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.72 (s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 149.84 (s), 146.21−145.65 (m), 144.18−143.56 (m), 142.87−142.28 (m), 140.79−139.30 (m), 136.95−136.03 (m), 135.78 (s), 131.04 (s), 122.89 (s), 112.08 (td, *J* = 16, 4 Hz), 110.29 (td, *J* = 18, 4 Hz); ^{19}F NMR ($CDCl_3$, 282 MHz): δ −139.85 − −140.06 (m, 4F), −142.18 − −142.41 (m, 2F), −150.46 (t, *J* = 21.0 Hz, 1F), −150.65 (t, *J* = 21.0 Hz, 2F), −159.68 − −160.11 (m, 6F); HRMS-APCI (*m*/*z*): $[M]^+$ calcd for $C_{24}H_2F_{15}NO_2$, 620.98405; found, 620.98489.

Synthesis of 2,6-(C_6F_5)$_2$-4-BrC_6H_2Cl (4). To a solution of C_6F_5MgBr in THF (50 mL), prepared as described for the synthesis of **1** from magnesium turnings (0.568 g, 23.4 mmol), was added 1,2-$Br_2C_2H_4$ (1.01 g, 5.4 mmol) and C_6F_5Br (4.45 g, 18 mmol) over anhydrous copper(I) bromide (3.87 g, 27 mmol), placed under argon atmosphere, in a 250 mL three-necked, round-bottom flask fitted with a reflux condenser, argon inlet, and dropping funnel. The brown suspension was stirred at rt for 30 min, and afterward, dioxane (6 mL) was added and the resulting gray suspension was stirred at rt for another 30 min. To this suspension was added a solution of **16** (1.772 g, 5 mmol) in toluene (50 mL). The reaction mixture was stirred at 95 °C (oil bath temperature) for a total of 11 h over 2 days. The reaction mixture was filtered through an approximately 6 cm thick pad of silica gel. The solvents were removed from the filtrate using a rotary evaporator, resulting a brown oil. Separation by column chromatography with petroleum ether using silica gel as stationary phase afforded **4** (1.02 g, 39%) as a colorless oil, which solidified upon addition of ethanol, and **1** (0.300 g, 10%) as side product. Mp 111−113 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.62 (s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 144.28 (dm, *J* = 250 Hz), 141.95 (dm, *J* = 256 Hz), 137.96 (dm, *J* = 250 Hz), 136.18 (s), 134.09 (s), 128.93 (s), 120.58 (s), 112.03 (td, *J* = 19, 4 Hz); ^{19}F NMR ($CDCl_3$, 282 MHz): δ −138.92 − −139.17 (m, 4F), −152.06 (tt, *J* = 21, 2 Hz, 2F), −160.87 − −161.12 (m, 4F); HRMS-APCI (*m*/*z*): $[M]^+$ calcd for $C_{18}H_2BrClF_{10}$, 521.88632; found, 521.88890.

Synthesis of 2,6-(C_6F_5)$_2$-4-Br$C_6H_2NO_2$ (5). To a solution of C_6F_5MgBr in THF (60 mL), prepared as described for the synthesis of **1** from magnesium turnings (0.410 g, 16.9 mmol), was added 1,2-$Br_2C_2H_4$ (0.732 g, 3.9 mmol) and C_6F_5Br (3.21 g, 13 mmol) over anhydrous copper(I) bromide (2.79 g, 19.5 mmol), placed, under argon atmosphere, in a 250 mL three-necked, round-bottom flask fitted with a reflux condenser, argon inlet, and a dropping funnel. The brown suspension was stirred at rt for 30 min; afterward, dioxane (6 mL) was added and the resulting gray suspension was stirred at rt for another 30 min. To this suspension was added a solution of **17** (1.800 g, 5 mmol) in toluene (60 mL). The reaction mixture was stirred at 95 °C (oil bath temperature) for approximately 4 h and at rt overnight. The contents of the flask were filtered through an approximately 6 cm thick pad of silica gel. The solvents were removed from the filtrate using a rotary evaporator. The residue was triturated with approximately 30 mL of petroleum ether, and then the solvent was removed to leave a slightly yellow solid. The solid was heated at 85−95 °C (2×10^{-2} mbar) in a sublimation apparatus to remove decafluorobiphenyl. Further heating at 120 °C (2×10^{-2} mbar) afforded the sublimation of **5** (2.048 g, 77%) as a light yellow solid. Mp 147−149 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.76 (s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 148.92 (s), 144.18 (dm, *J* = 250 Hz), 142.23 (dm, *J* = 258 Hz), 137.97 (dm, *J* = 252 Hz), 136.89 (s), 126.38 (s), 123.71 (m), 109.90 (td, *J* = 18, 4 Hz); ^{19}F NMR ($CDCl_3$, 282 MHz): δ −139.75 − −139.95 (m, 4F), −150.62 (tt, *J* = 21, 2 Hz, 2F), −159.92 − −160.16 (m, 4F); HRMS-APCI (*m*/*z*): $[M]^+$ calcd for $C_{18}H_2BrF_{10}NO_2$, 532.91037; found 532.91106.

Synthesis of 2,4,6-(C_6F_5)$_3$$C_6H_2NH_2$ (6). To a solution of **3** (3.790 g, 6.1 mmol) in ethanol (75 mL) was added iron powder (1.370 g, 24.4 mmol) and glacial acetic acid (4.2 mL). The mixture was vigorously stirred at 70 °C for 3 h, and afterward, all volatiles were removed with a rotary evaporator. Over the red residue was added dichloromethane (50 mL), and the suspension was filtered through a pad of Celite. The filtrate was washed with 3×10 mL of distilled water, and the organic fraction was dried on Na_2SO_4 and filtered. Removal of the solvent afforded **6** (3.48 g, 98%) as an off-white solid. Mp 171−173 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.33 (s, 2H, C*H*), 3.80 (br, 2H, N*H*); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 146.58−145.71

(m), 144.04 (s), 143.68−142.43 (m), 142.35−141.74 (m), 140.3−139.48 (m), 138.98−138.38 (m), 136.93−136.12 (m), 134.90 (s), 116.41 (s), 114.40 (td, *J* = 17, 4 Hz), 112.79 (s), 111.64 (td, *J* = 19, 4 Hz); ^{19}F NMR ($CDCl_3$, 282 MHz): δ −138.30 − −138.54 (m, 4F), −143.57 (dd, *J* = 23, 8 Hz, 2F), −152.68 (t, *J* = 21 Hz, 2F), −155.51 (t, *J* = 21 Hz, 1F), −160.17 − −160.41 (m, 4F), −161.90 − −162.13 (m, 2F); ^{1}H NMR ($(CD_3)_2CO$, 300 MHz): δ 7.50 (s, 2H, C*H*), 5.35 (br, 2H, N*H*); ^{13}C NMR ($(CD_3)_2CO$, 75 MHz): δ 147.87−147.31 (m), 147.19 (s), 147.05−146.57 (m), 144.57−144.07 (m), 144.01−143.36 (m), 142.77−142.10 (m), 141.00−140.08 (m), 139.54−138.85 (m), 137.69−136.88 (m), 135.61 (s), 115.93 (td, *J* = 17, 4 Hz), 114.71 (s), 113.35 (td, *J* = 20, 4 Hz), 112.46 (s); ^{19}F NMR ($(CD_3)_2CO$, 282 MHz): δ −141.07 (dd, *J* = 23, 8 Hz, 4F), −145.23 (dd, *J* = 23, 8 Hz, 2F), −157.97 (t, *J* = 21 Hz, 2F), −159.16 (t, *J* = 21 Hz, 1F), −164.28 − −164.57 (m, 4F), −164.85 − −165.11 (m, 2F); HRMS-APCI (*m*/*z*): $[M]^+$ calcd for $C_{24}H_4F_{15}N$, 591.00987; found, 591.00913; $[M + H]^+$ calcd for $C_{24}H_5F_{15}N$, 592.01770; found, 592.01652.

Synthesis of 2,6-$(C_6F_5)_2$-4-Br$C_6H_2NH_2$ (7). To a solution of **5** (1.000 g, 1.87 mmol) in ethanol (50 mL) was added iron powder (0.419 g, 7.5 mmol) and glacial acetic acid (1.3 mL). The mixture was vigorously stirred at 70 °C for 3 h, and afterward, all volatiles were removed with a rotary evaporator. Over the red residue was added dichloromethane (40 mL), and the suspension was filtered through a pad of Celite. The filtrate was washed with 3 × 10 mL of distilled water, and the organic fraction was dried on Na_2SO_4 and filtered. After evaporation of the solvent at reduced pressure, the oily residue was triturated with 3 mL of cold pentane. The solution was decanted off, and the remaining solid was washed with cold pentane (2 × 2 mL). The solid was dried at reduced pressure to obtain **7** (0.647 g, 72%) as a white solid. Mp 136−138 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.33 (s, 2H, C*H*), 3.58 (s, 2H, N*H*); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 144.51 (dm, *J* = 250 Hz), 143.67−143.07 (m), 142.50 (s), 140.32−139.54 (m), 136.90−136.18 (m), 135.52 (s), 114.27 (s), 111.19 (td, *J* = 19, 4 Hz), 109.79 (s); ^{19}F NMR ($CDCl_3$, 282 MHz): δ −138.40 (dd, *J* = 23, 8 Hz, 4F), −152.40 (t, *J* = 21 Hz, 2F), −160.04 − −160.32 (m, 4F); HRMS-APCI (*m*/*z*): $[M]^+$ calcd for $C_{18}H_4BrF_{10}N$, 502.93620; found, 502.93597; $[M + H]^+$ calcd for $C_{18}H_5BrF_{10}N$, 503.94402; found, 503.94338.

Synthesis of 2,4,6-$(C_6F_5)_3C_6H_2I$ (8). A 50 mL round-bottom flask was charged with **6** (0.39 g, 0.57 mmol) acetonitrile (8 mL) and 12 M HCl (0.2 mL; 2.40 mmol). The mixture was cooled to −15 °C in an ice-salt bath. A solution of sodium nitrite (0.079 g, 1.14 mmol) in water (0.3 mL) was added dropwise to the reaction mixture. The resulting yellow solution was stirred at −15 °C for a time not exceeding 5 min, and a solution of KI (0.237 g, 1.43 mmol) in water (0.3 mL) was added. Longer reaction times lead to the formation of 1,3,5-$(C_6F_5)_3C_6H_3$ as side product. The reaction mixture was stirred for 15 min at −15 °C and another 30 min at rt, and afterward, water (40 mL) was added. The formed precipitate was filtered, washed with 3 × 15 mL of water, and then collected from the glass frit and dried at reduced pressure. Sublimation at 130 °C (2 × 10^{-2} mbar) afforded **8** (0.345 g, 86%) as a white solid. Mp 180−182 °C; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.45 (s, 2H); ^{13}C NMR ($CDCl_3$, 151 MHz): δ 145.21−144.78 (m), 143.56−143.14 (m), 143.05−142.68 (m), 142.41−142.04 (m), 141.35−140.98 (m), 140.68−140.34 (m), 140.68−140.34 (m), 137.61−137.03 (m), 135.54 (s), 133.34 (s), 127.73 (s), 117.97 (td, *J* = 19, 4 Hz), 113.17 (td, *J* = 16, 4 Hz), 107.14 (s); ^{19}F NMR ($CDCl_3$, 565 MHz): δ −138.95 (dd, *J* = 22, 7 Hz, 4F), −142.56 (dd, *J* = 22, 8 Hz, 2F), −152.36 (t, *J* = 21 Hz, 2F), −152.46 (t, *J* = 21 Hz, 1F), −160.61 − −160.81 (m, 2F), −160.82 − −160.98 (m, 4F); HRMS-APCI (*m*/*z*): $[M]^+$ calcd for $C_{24}H_2F_{15}I$, 701.89562; found, 701.89714.

Synthesis of [2,4,6-$(C_6F_5)_3C_6H_2NCMe]_2$ (9). A 250 mL, three-necked, round-bottom flask fitted with a reflux condenser, argon inlet, and dropping funnel was charged with **6** (2.40 g, 4 mmol) and TsOH·H_2O (190 mg, 1.00 mmol). The installation was evacuated and refilled with argon (repeated twice), and then, activated 4 Å molecular sieves, dry toluene (100 mL), and 2,3-butandione (172 mg, 2.00 mmol) were added and the mixture was heated to 85 °C (oil bath temperature) for 10 h and then at 130 °C over 2 days. At this time two reaction products formed but the aniline was still present (verified by TLC). As a consequence, more TsOH·H_2O (190 mg, 1.00 mmol) was added together with additional 4 Å molecular sieves and the mixture was heated to 130 °C over another 3 days. The molecular sieves were removed by filtration, the solution was washed with water (2 × 20 mL), and the organic phase was separated and dried on Na_2SO_4. The residue obtained after filtration and solvent removal was dissolved in ethanol and cooled to 0 °C. The precipitate was filtered and washed with a small amount of chloroform and then with pentane, and was dried at reduced pressure to give **9** (205 mg, 8%) as a yellow solid. Mp 295−297 °C; ^{1}H NMR ($(CD_3)_2CO$, 300 MHz): δ 7.86 (s, 4H, C*H*), 1.66 (s, 6H, CH_3); ^{13}C NMR ($(CD_3)_2CO$, 75 MHz): δ 170.52 (s), 149.49 (s), 147.42−146.68 (m), 146.31−145.78 (m), 144.23−143.03 (m), 143.06−142.44 (m), 140.91−139.62 (m), 137.60−136.47 (m), 135.97 (s), 123.96 (s), 118.14 (s), 114.84 (td, *J* = 17, 4 Hz), 113.19 (td, *J* = 19, 3 Hz), 16.27 (s); ^{19}F NMR ($(CD_3)_2CO$, 282 MHz): δ −139.38 (dd, *J* = 22, 6 Hz, 4F), −142.94 (dd, *J* = 22, 5 Hz, 4F), −144.68 (dd, *J* = 22, 8 Hz, 4F), −155.59 (t, *J* = 15 Hz, 4F), −157.03 (t, *J* = 21 Hz, 2F), −163.53 − −163.87 (m, 4F), −164.21 − −164.67 (m, 8F); HRMS-APCI (*m*/*z*): $[M + H]^+$ calcd for $C_{52}H_{11}F_{30}N_2$, 1233.04377; found, 1233.04513.

Synthesis of 2,4,6-$(C_6F_5)_3C_6H_2$NHC(O)H (10). A 10 mL round-bottom flask was charged with **6** (118 mg, 0.2 mmol) and formic acid (3 mL). The flask was fitted with a reflux condenser, and the mixture was heated at 70 °C (oil bath temperature) for 5 h. After approximately 2.5−3 h, a white precipitate formed. All volatiles were removed at reduced pressure. The product was separated by column chromatography with dichloromethane using silica gel as stationary phase. Removal of the solvent afforded **10** (103 mg, 83%) as an off-white solid. Mp 221−223 °C; ^{1}H NMR ($(CD_3)_2CO$, 400 MHz): δ *Z* isomer 9.26 (s, 1H, N*H*), 7.97 (s, C(O)*H*), 7.91 (s, C*H*); *E* isomer 9.11 (br, 0.13H, N*H*), 7.99 (s, C*H*), 7,95 (br, C(O)*H*); ^{13}C NMR ($(CD_3)_2CO$, 101 MHz): δ 163.15 (s), 159.73 (s), 159.65 (s), 146.77−146.35 (m), 144.31−143.93 (m), 143.53−142.91 (m), 141.02−140.42 (m), 140.39−139.72 (m), 137.92−137.22 (m), 137.07 (s), 136.95 (s), 136.45 (s), 135.65 (s), 126.78 (s), 126.50 (s), 126.09 (s), 114.86 (td, *J* = 17, 4 Hz), 113.95 (td, *J* = 19, 4 Hz); ^{19}F NMR ($(CD_3)_2CO$, 376 MHz): δ *Z* isomer −141.38 − −141.53 (m, 4F), −156.75 (t, *J* = 21 Hz, 0.96F), −157.10 (t, *J* = 20 Hz, 2.01F), −164.50 − −164.70 (m, 3.81F); *E* isomer −141.08 − −141.24 (m, 0.52F), −155.78 (t, *J* = 20 Hz, 0.25F), −156.47 (t, *J* = 21 Hz, 0.12F), −163.62 − −163.83 (m, 0.47F); overlapped resonance signals of *Z* and *E* isomers −144.40 − −144.56 (m, 2.16F), −164.12 − −164.39 (m, 2.04F); ^{1}H NMR (C_6D_6, 600 MHz): δ *E* isomer 7.66 (d, *J* = 10 Hz, 0.21H, C(O)*H*), 7.28 and 7.27 (d corresponding to N*H* overlapped with the singlet corresponding to C*H*, 0.75H); *Z* isomer 7.35 (s, C*H*, 2H), 7.11 (s, C(O)*H*, 1.15H), 5.76 (s, N*H*, 1H); ^{19}F NMR (C_6D_6, 565 MHz): δ *E* isomer −140.52 − −140.64 (m, 0.85F), −143.68 (dd, *J* = 23, 7 Hz, 0.43F), −151.07 (t, *J* = 22 Hz, 0.39F), −152.91 (t, *J* = 22 Hz, 0.21F), −159.85 − −160.04 (m, 0.73F), −160.90 − −161.05 (m, 0.37F); *Z* isomer −140.24 (dd, *J* = 23, 7 Hz, 4F), −143.57 (dd, *J* = 23, 8 Hz, 2F), −153.04 (t, *J* = 22 Hz, 1.90F), −153.39 (t, *J* = 22 Hz, 0.95F), −161.19 − −161.37 (m, 5.24F); ^{1}H NMR ($CDCl_3$, 600 MHz): δ *Z* isomer 7.96 (s, 1H, C(O)*H*), 7.62 (s, 2H, C*H*), 7.03 (s, 1H, N*H*); *E* isomer 7.80 (d, *J* = 10 Hz, 0.56H, C(O)*H*), 7.65 (s, 1.25H, C*H*), 7.06 (d, *J* = 11 Hz, 0.6H, N*H*); ^{19}F NMR ($CDCl_3$, 565 MHz): δ *Z* isomer −139.93 (dd, *J* = 22, 7 Hz, 4F), −142.62 (dd, *J* = 23, 8 Hz), −152.13 (t, *J* = 21 Hz), −152.63 (t, *J* = 21 Hz, 0.92F), −160.67 − −160.82 (m, 1.70F); *E* isomer −139.59 (dd, *J* = 22, 7 Hz, 2.44F), −142.69 (dd, *J* = 27, 8 Hz), −150.64 (t, *J* = 21 Hz, 1.15F), −152.05 (t, 21 Hz), −159.24 − −159.43 (m, 2.13F); overlapped resonance signals of *Z* and *E* isomers −160.27 − −160.54 (m, 4.50F); IR (KBr pellet, *υ*, cm^{-1}): 3231 (br, NH), 2886 (s, CH carbonyl) 1705 (s, CO); HRMS-APCI (*m*/*z*): $[M + H]^+$ calcd for $C_{25}H_5F_{15}NO$, 620.01261; found, 620.01513.

Synthesis of 2,4,6-$(C_6F_5)_3C_6H_2$NC (11). Under argon atmosphere, to a solution of **10** (204 mg, 0.33 mmol) in anhydrous $CHCl_3$ (20 mL) was added triethylamine (191 mg, 1.89 mmol), and afterward, the mixture was cooled to 0 °C on an ice bath. *Via* syringe, $POCl_3$ (124 mg, 0.80 mmol) was carefully added dropwise. The reaction mixture was allowed to reach rt and was stirred for another 72 h. Afterward, a 1.5 M solution of Na_2CO_3 (10 mL) was added. After

30 min of stirring, the organic fraction was separated, washed with water (3 × 10 mL), dried over Na_2SO_4, and filtered. The solvent was removed at reduced pressure using a rotary evaporator. Separation by column chromatography with petroleum ether/ethyl acetate 5/0.5 using silica gel as stationary phase afforded **11** (192 mg, 97%) as a white solid. Mp 189−191 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.68 (s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 173.79 (s), 146.34−145.66 (m), 144.49−143.83 (m), 143.82−143.03 (m), 143.04−142.34 (m), 141.09−140.39 (m), 140.37−139.54 (m), 137.08−136.17 (m), 134.72 (s), 128.53 (s), 127 (s), 126.40 (s), 112.61 (td, J = 16, 4 Hz), 110.31 (td, J = 18, 4 Hz); ^{19}F NMR ($CDCl_3$, 282 MHz): δ −138.85 to −139.10 (m, 4F), −142.47 to −142.68 (m, 2F), −150.35 (t, J = 21 Hz, 2F), −151.33 (t, J = 21 Hz, 1F), −159.82 to −160.08 (m, 4F), −160.08 to −160.32 (m, 2F); IR (KBr pellet, υ, cm^{-1}): 2121 (s, NC); HRMS-APCI (m/z): [M + H]$^+$ calcd for $C_{25}H_3F_{15}N$, 602.00205; found, 602.00107.

Synthesis of 1,3,5-$(C_6F_5)_3C_6H_3$ (12). A 100 mL round-bottom flask was charged with **6** (887 mg, 1.5 mmol) and 95% sulfuric acid (13 mL), and the mixture was stirred until all aniline derivative had dissolved. Sodium nitrite (311 mg, 4.5 mmol) was added portion-wise, and afterward the reaction mixture was heated at 50 °C for 3 h. After the mixture was cooled to rt, copper(I) iodide (855 mg, 4.5 mmol) was added portion-wise. When the evolution of nitrogen ceased, the stirring was continued at 50 °C for another 3 h. The reaction mixture was poured in water with ice and extracted with diethyl ether (3 × 25 mL) and dichloromethane (2 × 30 mL). The organic fractions were combined, washed with a 5% (w/v) sodium sulfite solution (50 mL) and distilled water (50 mL), and dried over Na_2SO_4. After filtration and evaporation of the solvents, the resulting solid was dried at reduced pressure and heated at 90 °C (2 × 10^{-2} mbar) in a sublimation apparatus to remove volatile impurities. Further heating at 160 °C (2 × 10^{-2} mbar) allowed the sublimation of a slightly yellow solid. This solid was collected and washed with pentane (6 × 5 mL). After drying at reduced pressure, **12** (692 mg, 80%) remained as a white solid. Mp 234−236 °C (232−236 °C lit.);[37] ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.63 (s, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 144.36 (dm, J = 249), 141.23 (dm, J = 255 Hz), 138.20 (dm, J = 254 Hz), 132.79 (s), 127.99 (s), 114.26 (td, J = 17, 4 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz): δ −142.87 (dd, J = 23, 8 Hz, 6F), −153.31 (t, J = 21 Hz, 3F), −160.96 to −161.14 (m, 6F); HRMS-APCI (m/z): [M]$^+$ calcd for $C_{24}H_3F_{15}$, 575.99897; found, 575.99800.

Synthesis of 2,4,6-$(C_6F_5)_3C_6H_2Si(H)Me_2$ (13). A 50 mL Schlenk flask charged with **8** (318 mg, 0.45 mmol) was evacuated and backfilled with argon (the cycle was performed three times); then hexane (20 mL) was added, the solution was cooled to −78 °C, and a 2.5 M *n*BuLi solution in hexane (0.4 mL, 1.0 mmol) was added. The reaction was stirred at −78 °C and, after 2 h, $Me_2Si(H)Cl$ (189 mg, 2.0 mmol) was introduced. After 30 min the cooling bath was removed and the reaction mixture was stirred at rt for another hour. The content of the flask was transferred to a separatory funnel. Water (15 mL) and Et_2O (15 mL) were added, and the organic layer was separated and washed with water (3 × 15 mL). The organic layer was dried over Na_2SO_4 and filtered, and the solvents were evaporated. The residue was separated by column chromatography with hexane using alumina as stationary phase to afford **13** (210 mg, 74%) as a white solid. Mp 117−119 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.43 (s, 2H), 3.87 (s, 1H), −0.02 (d, J = 4 Hz, 6H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 145.90−145.40 (m), 143.46−142.24 (m), 141.10 (s), 140.53−139.68 (m), 139.66−138.81 (m), 137.26−136.21 (m), 134.40 (s), 133.25 (s), 128.44 (s), 116.27 (td, J = 20, 4 Hz), 113.75 (td, J = 16, 4 Hz), −3.48 (s); ^{19}F NMR ($CDCl_3$, 376 MHz): δ −138.84 (dd, J = 23, 8 Hz), −142.66 (dd, J = 23, 8 Hz), −153.12 (t, J = 21 Hz), −153.21 (t, J = 21 Hz), −161.12 (td, J = 22, 8 Hz), −161.37 (dt, J = 23, 8 Hz); ^{29}Si NMR ($CDCl_3$, 79 MHz): δ −19.09 (s); IR (KBr pellet, υ, cm^{-1}): 2174 (s, SiH). HRMS-APCI (m/z): [M − H]$^+$ calcd for $C_{26}H_8F_{15}Si$, 633.01503; found, 633.01417.

Synthesis of 2,4,6-$(C_6F_5)_3C_6H_2Si(Cl)Me_2$ (14). A 50 mL Schlenk flask charged with **13** (710 mg, 1.12 mmol) was evacuated and refilled with argon (repeated three times), and then dry dichloromethane (10 mL) and SO_2Cl_2 (1 mL, approximately 12 mmol) were added. After stirring for 17 h at rt, all volatiles were evaporated at reduced pressure. Product **14** was obtained as a white moisture sensitive solid. Mp 152−154; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.45 (s, 2H), 0.30 (s, 6H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 146.13−145.36 (m), 143.62−142.33 (m), 140.80−140.30 (m), 140.30−139.83 (m), 139.34 (s), 139.74−138.93 (m), 137.24−136.40 (m), 134.22 (s), 134.15 (s), 129.30 (s, J = 13.4 Hz), 116.51 (td, J = 20, 4 Hz), 113.29 (td, J = 16, 4.0 Hz), 4.47 (s); ^{19}F NMR ($CDCl_3$, 376 MHz): δ −138.11 to −138.66 (m, 4F), −142.39 to −142.70 (m, 2F), −152.33 to −152.71 (two overlapped triplets, 3F), −160.76 to −161.00 (m, 2F), −161.00 to −161.27 (m, 4F); ^{29}Si NMR ($CDCl_3$, 79 MHz): δ 18.67 (s); HRMS-APCI (m/z): [M − Cl]$^+$ calcd for $C_{26}H_8F_{15}Si$, 633.01503; found, 633.01489.

Synthesis of 2,4,6-$(C_6F_5)_3C_6H_2Si(F)Me_2$ (15). Under argon atmosphere, a solution of $TlPF_6$ (124 mg, 0.35 mmol) in dry acetonitrile (3 mL) was added via syringe to **14** (237 mg, 0.35 mmol) dissolved in dry acetonitrile (3 mL). A white precipitate formed instantly. The reaction mixture was stirred overnight at rt. The clear solution was separated from the decanted precipitate, which was washed with dry toluene (6 mL). After the evaporation of all volatiles at reduced pressure from the combined solutions, **15** (225 mg, 97%) was obtained as a white solid. Mp 125−127 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.45 (s, 2H), 0.14 (d, 6H, $^3J_{F,H}$ = 8 Hz); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 145.90−145.43 (m), 143.44−142.42 (m), 140.49−139.87 (m), 139.61−139.25 (m), 139.18−138.78 (m), 137.14−136.70 (m), 136.66−136.32 (m), 133.68−133.62 (two s overlapped), 129.15, 116.13 (td, J = 20, 3 Hz), 113.49 (td, J = 16, 4 Hz), 0.17 (d, J = 15.2 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz): δ −139.07 (dd, J = 23.1, 8.3 Hz, 4F), −142.39 to −142.99 (m, 2F), −152.75 (t, J = 20.6 Hz, 1 F), −152.87 (d, J = 20.9 Hz, 2F), −155.63 (s, 1F), −160.87 to −161.06 (m, 2F), −161.35 to −161.54 (m, 4F); ^{29}Si NMR ($CDCl_3$, 79 MHz): δ 21.24 (d, $^1J_{Si,F}$ = 280 Hz); HRMS-APCI (m/z): [M]$^+$ calcd for $C_{26}H_8F_{16}Si$, 652.01343; found, 652.01504.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H, ^{13}C and ^{19}F NMR and HRMS spectra, crystal data, refinement details, depiction of the C−F···π and F···H−C interactions, CIFs, coordinates of the calculated molecular structures for Z and E isomers of 2,6-$(C_6F_5)_2C_6H_3NHC(O)H$, **13**, 2,6-$(2,6\text{-}X_2C_6H_3)_2C_6H_3Si(H)Me_2$ (X = F, Me) and of the corresponding silylium ions. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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