Reactions of Bifunctional Perfluoroaryl silanes with Activated C–F Bonds in Perfluorinated Arenes

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ABSTRACT: Reactions of bifunctional perfluoroaryl silanes, p- and m-C₆F₅(SiMe₃)₂ as well as o-BrC₆F₅SiMe₃ with substituted perfluoroarenes having electron-withdrawing groups were investigated using NMR and density functional theory calculation techniques. The C–F bond in perfluoroarenes was activated by the para-position of an electron-withdrawing group, such as CF₃, C₆F₅, CN, and NO₂. The reaction of C₆F₅(SiMe₃)₂ mainly occurred at the para-position of the perfluoroarenes and also occurred at the ortho-position of C₆F₅CN and C₆F₅NO₂. Two equivalent reactions of perfluoroarenes with bifunctional p- and m-C₆F₅(SiMe₃)₂ provided disubstituted perfluoroarenes, along with a small amount of protonated monosubstituted perfluoroarenes. The reaction of o-BrC₆F₅SiMe₃ with the CF₃- and CN-substituted pentafluorobenzenes provided unexpected coupling products between C–Br and C–F bonds, in addition to the coupling products between C–SiMe₃ and C–F bonds.

INTRODUCTION

Fluorinated aromatic compounds are expected to have unique physical properties because of the π-electron system connected with fluorine atoms, which bring high electronegativity, low polarization, and high bond energy to the C–F bond. Especially, bifunctional perfluoroaryl units can be the basic skeleton for developing materials that have peculiar properties. Past research on fluorinated materials has explored a variety of applications. Partially fluorinated poly(arylene ether)s have been developed for application as fuel cell membranes, and their polymerisability and degradation during sulfonation were examined. A wide variety of bifunctional phenyl ethers having tetrafluorophenylene or octafluorobiphenylene moieties has been synthesized for optical or membrane applications. Tetrafluorophenylene-bridged bisphospholes were synthesized to analyze their photophysical and electrochemical properties. Similar perfluoroaromatic molecules have been explored for application to peptides and proteins; model cysteine compounds were prepared by nucleophilic aromatic substitution (SNAr) with hexafluorobenzene and decfluoroarylphenyl to study stapled peptides. Perfluoroaromatic linkers have also been introduced to the backbones of model peptides.

The π-electron system associated with fluorine atoms has interesting properties involved in molecular recognition and electron transfer. Derivatives of decfluorobiphenyl and octafluoronaphthalene could act as acceptors for an anion due to anion–π interaction. Polyfluorinated oxacalixarenes, which are potential macrocyclic molecules to make “guest–host” complexes, have been synthesized by reaction of perfluoro-m-xylene with tetrafluorexoroscinol. Aiming for use as organic conductors in printable electronics, perfluoroarylene and octafluoroarylene dendrimers, which were synthesized and examined for an electron-transport layer and an n-type semiconductor. Therefore, the development of synthetic methods utilizing

Received: October 4, 2019
Accepted: October 30, 2019
Published: November 26, 2019
bifunctional perfluoraryl units is in demand by a number of industrial fields.

We have been investigating the trimethylsilyl-based transfer reagent based on a pentafluorophenyl unit, C₆F₅SiMe₃. The C≡O bond of hexafluoroacetone reacts with C₆F₅SiMe₃ to give perfluorinated aromatic ether by further reaction with C₆F₅CH₂Br.¹¹ Both the C≡N bonds of perfluorinated cyclic imines² and C≡C bonds of highly branched perfluoroolefins⁰ reacted with C₆F₅SiMe₃ to give the corresponding pentafluorophenyl cyclic imines and olefins via an addition–elimination (Adₜ,E) mechanism. Interestingly, the para-position of the introduced C₆F₅ group in the resulting cyclic imines and olefins could react further with C₆F₅SiMe₃ molecules to provide perfluorophenyl and/or perfluoroterphenyl products. In cases of perfluorinated aromatic compounds containing electron-withdrawing substituents, this multiple pentafluoroarylation occurred at both the para- and ortho-positions of the electron-withdrawing substituents, resulting in not only para-phenylenes but also m-phenylenes.¹⁴

A bifunctional trimethylsilyl-based tetrafluorophenylene transfer reagent, p-C₆F₅(SiMe₃)₂, has been prepared from p-C₆F₅Br₂ with moderate yields.¹⁵ Both trimethylsilyl sites reacted with aromatic aldehydes to provide diols having the tetrafluorophenylene skeleton.¹⁶ However, reactions of p-C₆F₅(SiMe₃)₂ with fluorinated compounds, which may exploit the π-electron system associated with fluorene atoms, have not been reported. In the present study, we suggest synthetic methods for introducing a perfluoroaryl moiety into perfluoroarenes and investigate reactions of several perfluoroarenes containing electron-withdrawing substituents with p-C₆F₅(SiMe₃)₂. In addition, preparation of geometrical isomers of C₆F₅(SiMe₃)₂, which have not yet been reported, is examined to expand the range of potential methods to introduce the tetrafluorophenylene moiety.

## RESULTS AND DISCUSSION

By modification of the Ruppert method for C₆F₅SiMe₃, 1,4-bis(trimethylsilyl)tetrafluorobenzene [p-C₆F₅(SiMe₃)₂] has been prepared using ClSiMe₃ and P(NEt₂)₃.¹⁵ In this present method, although an excess of ClSiMe₃ and P(NEt₂)₃ was used in refluxing hexane, the desired product was obtained at relatively low yields. In the present study, anhydrous CH₂CN at a lower reaction temperature (−30 °C) was used to prepare C₆F₅(SiMe₃)₂ from C₆F₅Br₂. Using this lower reaction temperature, p-C₆F₅(SiMe₃)₂ could be obtained at higher yields than with the previous method. As shown in our previous study,¹⁴ pentafluorophenylation using C₆F₅SiMe₃ could not progress for perfluoroarenes having an electron-releasing substituent. Therefore, we focused on four perfluoroarenes having electron-withdrawing substituents (X = CF₃, C₆F₅O, CN, and NO₂) for the reaction of p-C₆F₅(SiMe₃)₂ (Scheme 1). The results are summarized in Table 1.

Besides pentafluorophenylation using C₆F₅SiMe₃, nucleophilic attack occurred only at the para-position of C₆F₅CF₃ (1a). The reaction mixture of 1a with p-C₆F₅(SiMe₃)₂ became a white suspension, with p-C₆F₅(p-C₆F₅CF₃)₂ (4a) as a component of the suspended phase. The disubstituted product 4a was obtained by the reaction of both SiMe₃ groups of p-C₆F₅(SiMe₃)₂ with 1a via an addition–elimination (Adₜ,E) mechanism.¹²⁻¹⁵ After removing the white precipitate, the filtrate DMF solution contained a mixture of 4a and 4'-H(C₆F₅)(p-C₆F₅CF₃) (3a). Evaporation and successive Kugelrohr distillations provided both 3a and 4a as the isolated form. However, the protonated monosubstituted product 3a was obtained at very low yield because it was distilled out along with the DMF solvent. The protonated monosubstituted product 3a formed from the trimethylsilylated monosubstituted product, p-Me₅Si(C₆F₅)(C₆F₅CF₃) 2a, which was not stable enough to isolate. Thus, it was necessary to modify 4a by successive Adₜ,E reactions with 1a and produce 3a by protonation.

The above reaction of p-C₆F₅(SiMe₃)₂ could apply to C₆F₅CF₃ (1b), which is a perfluoroarene having an aromatic C₆F₅ group as the electron-withdrawing substituent instead of the CF₃ group. Similar to 1a, both C–SiMe₃ bonds of p-C₆F₅(SiMe₃)₂ reacted with 1b to produce linear p-(C₆F₅)(p-C₆F₅CF₃)₂ (2b) predominately. Since the disubstituted product 2b had lower solubility in DMF, 2b was easily collected as a precipitate from the reaction mixture. Mean-

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Table 1. Reaction of 1,4-Bis(trimethylsilyl)tetrafluorobenzene [p-C₆F₅(SiMe₃)₂] with Perfluoroarenes, 1⁵

| entry | aromatics | yield (%) |
|-------|-----------|-----------|
|       |           | monosubstituted | disubstituted |
| 1     | C₆F₅CF₃ (1a) | 3a (2) | 4a (32) |
| 2     | C₆F₅CF₃ (1b) | 3b (2) | 4b (25) |
| 3     | C₆F₅CN (1c) | 3c (16), 6c (<1%) | 4c (39), 7c (<1%) |
| 4     | C₆F₅NO₂ (1d) | 3d (8), 6d (1%) | 4d (22%), 7d (5%) |

The number-letter labels (e.g., 3a) refer to structures shown in Scheme 1 above. Isolated yield. Determined by ²⁹F NMR of Kugelrohr distillates.
while, the DMF solution filtered from the reaction mixture contained the starting material 1b and 4'-H(C_6F_4)(p-C_6F_4C_6F_3) (3b). Although the protonated monosubstituted product 3b was formed at very low yield according to 19F NMR of the DMF solution, 3b could be isolated by Kugelrohr distillation. In the reaction of 1b with C_6F_5SiMe_3, multiple pentafluorophenolization occurred at the terminal C=C bonds at the para-position, providing perfluorinated oligophenylene products. Both 3b and 4b had a reactive C=C bond for the 

scheme

4-\text{E}\ reaction; however, the reactions of p-C_6F_5SiMe_3 did not substantially occur for either 3b or 4b because the intermediate carbanion formed from p-C_6F_5SiMe_3 had lower nucleophilicity than that formed from C_6F_5SiMe_3.

As described in a previous report, reaction of C_6F_5CN (1c) with C_6F_5SiMe_3 occurred at both para- and ortho-positions of the CN group. Even though the first attack of C_6F_5SiMe_3 predominantly occurred at the para-position, the multiple pentafluorophenolization of C_6F_5SiMe_3 occurred at both the para-position of the introduced C_6F_5 ring and the ortho-position of the original C_6F_5CN ring. Therefore, the C_6F_5CN (1c) with excess C_6F_5SiMe_3 yielded the star-shaped 2,4,6-trisubstituted derivatives. In the present reaction of 1c with another C_6F_4(SiMe_3)2, however, the attack on the ortho-position of the CN group rarely occurred. Thus, the ortho-isomers, 4'-H(C_6F_4)(o-C_6F_5CN) (6c) and p-C_6F_5F(o-C_6F_5CN)(p-C_6F_5CN) (7c), were obtained as trace amounts in addition to the para-isomers, 4'-H(C_6F_4)(p-C_6F_5CN) (3c) and p-C_6F_5F(p-C_6F_5CN) (4c). At the same time, the yield of the protonated monosubstituted product 3c was much higher than those of 3a and 3b, while the yield of the disubstituted product 4c was comparable to those of 4a and 4b. Our previous report showed that the ortho-position of C_6F_5NO_2 (1d) was less reactive against C_6F_5SiMe_3 than that of 1c; the reaction of p-C_6F_5F(SiMe_3)_2 at the ortho-position of C_6F_5NO_2 (1d) also occurred. That is, the protonation of the silylated intermediate 2d provided 4'-H(C_6F_4)(p-C_6F_5FNO_2) (3d) as a major product, while 5d yielded 4'-H(C_6F_4)(o-C_6F_5FNO_2) (6d) as a minor product, similar to the case of 1c. Furthermore, the reaction of the intermediates 2d and 5d with another 1d molecule gave p-C_6F_5F(p-C_6F_5FNO_2) (4d) and p-C_6F_5F(o-C_6F_5FNO_2)(p-C_6F_5FNO_2) (7d) as major and minor products, respectively.

Next, to examine substituent effects of perfluoroarenes on product distribution, the syntheses and reactions of the positional isomer of C_6F_5(SiMe_3)_2 were investigated. As shown above, we improved the reaction procedure for the synthesis of p-C_6F_5(SiMe_3)_2 over a previous work. The improved reaction condition could apply to the meta-isomers of C_6F_5F(SiMe_3)_2; 1,3-bis(trimethylsilyl)tetrafluorobenzene [m-C_6F_5(SiMe_3)_2] was obtained from m-C_6F_5Br, at slightly lower yields than the para-isomer, p-C_6F_5(SiMe_3)_2. Reactions of the same perfluoroarenes, having electron-withdrawing substituents X (X = CF_3, C_6F_5, CN, and NO_2), with m-C_6F_5(SiMe_3)_2 were examined in this study (Scheme 2). The results are summarized in Table 2.

In the reaction of m-C_6F_5(SiMe_3)_2 with C_6F_5CF_3 (1a), only the para-position of the CF_3 group was sufficiently reactive for the nucleophile to produce m-C_6F_5F(p-C_6F_5CF_3) (10a) as a major product at 35% yield and 5'-H(C_6F_4)(p-C_6F_5CF_3) (9a) as a minor product at 4% yield. The protonated monosubstituted product 9a and the disubstituted product 10a were obtained from unstable monosubstituted silylate 8a by protonation and successive Ad_Q-E reactions, respectively. In

\[ \text{Scheme 2} \]

\[ \text{Table 2. Reaction of 1,3-Bis(trimethylsilyl)tetrafluorobenzene [m-C_6F_5(SiMe_3)_2] with Perfluoroarenes, 1^{a}} \]

| entry | aromatics | monosubstituted | disubstituted |
|-------|-----------|-----------------|---------------|
| 5     | C_6F_5CF_3 (1a) | 9a (4) | 10a (35) |
| 6     | C_6F_5CF_3 (1b) | 9b (8) | 10b (13) |
| 7     | C_6F_5CN (1c) | 9c (29), 12c (3') | 10c (39^{39}), 13c (3') |
| 8     | C_6F_5NO_2 (1d) | 9d (25'), 12d (6') | 10d (16'), 13d (9') |

\(^{a}\)The number-letter labels (e.g., 9a) refer to structures shown in Scheme 2 above.

\(^{b}\)Isolated yield. Determined by 19F NMR of Kugelrohr distillates. 6\% yield in pure form.

spite of the different SiMe3 positions in the bifunctional trimethylsilylated reagent, the product distribution in the reaction of m-C_6F_5(SiMe_3)_2 with 1a was almost the same as that of p-C_6F_5(SiMe_3)_2 with 1a. In the reaction of m-C_6F_5(SiMe_3)_2 with C_6F_5F(C_6F_5) (1b), the disubstituted product [m-(C_6F_5)(p-C_6F_5CF_3)] (10b) was obtained at 13% yield, almost half the yield of 4b, even though the yield of the protonated monosubstituted product [5'-H(C_6F_4)(p-C_6F_5CF_3)] (9c) increased slightly to 8% (Table 2, entry 6), compared with 2% of 3b (Table 1, entry 2).

In the reaction of m-C_6F_5(SiMe_3)_2 with C_6F_5CN (1c), even though the total yields of the monosubstituted product [5'-H(C_6F_4)(p-C_6F_5CN)] (9c) and the disubstituted product [m-C_6F_5(p-C_6F_5CN)] (10c) were almost the same as the total yields of 3c and 4c [from p-C_6F_5(SiMe_3)_2], the ratio between

DOI: 10.1021/acsomega.9b03273
ACS Omega 2019, 4, 20807–20818
20809
the monosubstituted and disubstituted products was different for the *para*- and *meta*-reagents. Thus, 9c and 10c were obtained evenly (29 and 27% for 9c and 10c, respectively; Table 3, entry 7), while the disubstituted 4c was preferred to

Table 3. Reaction of 1-Bromo-2-trimethylsilyl-3,4,5,6-tetrafluorobenzene (*o*-Br(C₆F₅)SiMe₃) with Perfluoroarenes, 1*

| entry | aromatics                   | yield (%)b | monosubstituted | disubstituted |
|-------|-----------------------------|------------|-----------------|--------------|
| 9     | C₆F₅CF₃ (1a)                | 14a (4)    | 15a (9)         |
| 10    | C₆F₅CF₃ (1b)                | 14b (8)    | 17b (10)       |
| 11    | C₆F₅CN (1c)                 | 14c (6)    | 15c (5)        |

The number-letter labels (e.g., 14a) refer to structures shown in Scheme 3 above. * Determined by ¹⁹F NMR of Kugelrohr distillates.

the monosubstituted 3c (39% for 4c vs 16% for 3c, Table 1, entry 3). At the same time, both 5'-H(C₆F₅)(*o*-C₆F₅CN) (12c) and m-C₆F₅(*o*-C₆F₅CN)(p-C₆F₅CN) (13c) were also formed at 3% yield for each (Run 7, Table 2) in contrast with the trace formation of the *ortho*-isomers, 4'-H(C₆F₅)(*o*-C₆F₅CN) (6c) and p-C₆F₅(*o*-C₆F₅CN)(p-C₆F₅CN) (7c). The increases of the protonated monosubstituted product and the *ortho*-positional isomers were more prominent in the reaction of m-C₆F₅(SiMe₃)₂ with C₆F₅NO₂ (1d). That is, the yield of 5'-H(C₆F₅)(p-C₆F₅NO₂) (9d) became larger than that of m-C₆F₅(p-C₆F₅NO₂) (10d), while yields of *ortho*-positional isomers [5'-H(C₆F₅)(p-C₆F₅NO₂) (12d) and m-C₆F₅(*o*-C₆F₅NO₂)(p-C₆F₅NO₂) (13d)] also increased. Therefore, the increase of *ortho*-positional isomers was caused by increasing stability of the silylated intermediate 11 because of resonance of the CN and NO₂ groups. In addition, the increase of the protonated monosubstituted product was caused by lowering the nucleophilicity of monosubstituted silylarene 8, becoming less reactive with other molecules.

Next, the reaction of *o*-C₆F₅Br₃ with ClSiMe₃ and P(NEt₂)₃ was examined for preparing *o*-C₆F₅(SiMe₃)₂, using the same preparation procedure as that of p-C₆F₅(SiMe₃)₂ and m-C₆F₅(SiMe₃)₂. Although the white crystalline material precipitated at −30 °C 3 h after the start of the reaction, no desired *o*-C₆F₅(SiMe₃)₂ was found in the precipitate, only 1-bromo-2-trimethylsilyl-3,4,5,6-tetrafluorobenzene (*o*-Br(C₆F₅)SiMe₃). Neither longer reaction time nor higher temperature decreased the yield of *o*-Br(C₆F₅)SiMe₃, even though both longer reaction time and higher temperature decreased the yield of *o*-Br(C₆F₅)SiMe₃ in the reaction. Furthermore, pure *o*-Br(C₆F₅)SiMe₃ could not be collected from the precipitate because it melted at ambient temperature. Vacuum distillation was not able to isolate *o*-Br(C₆F₅)SiMe₃ because the boiling point of the byproduct O=P(NEt₂)₃ is close to that of the desired *o*-Br(C₆F₅)SiMe₃. Therefore, reactions of the bifunctional trimethylsilylated reactent with perfluoroarenes were performed using *o*-Br(C₆F₅)SiMe₃, including 16 wt % of O=P(NEt₂)₃ (Scheme 3). The results are summarized in Table 3.

In the reaction with *o*-Br(C₆F₅)SiMe₃ the *para*-position of C₆F₅CF₃ (1a) reacted with the C–SiMe₃ bond while the adjacent C–Br bond was retained, giving a monosubstituted bromide [*o*-Br(C₆F₅)(p-C₆F₅CF₃)] (14a) at 16% yield (Table 3, entry 9). Very interestingly, the remaining C–Br bond successively reacted with another 1a molecule at the *para*-position to provide the disubstituted product [*o*-Br(C₆F₅)(p-C₆F₅CF₃)₂] (15a) at 9% yield. In the reaction of *o*-Br(C₆F₅)SiMe₃ with C₆F₅CF₃ (1b), monosubstituted bromide [*o*-Br(C₆F₅)(p-C₆F₅CF₃)] (14b) was formed at 8% yield (Table 3, entry 10). Even after the Kugelrohr distillation, however, 14b was only obtained as the mixed form with the protonated monosubstituted product [6'-H(C₆F₅)(p-C₆F₅ CF₃) (17b)]. The formation of 17b indicates that the C–Br bond again participated in the Ar–Ar coupling reaction with a yet unknown mechanism, probably through the intermediate 16b. Meanwhile, the reaction of *o*-Br(C₆F₅)SiMe₃ with C₆F₅CN (1c) gave a monosubstituted bromide [*o*-Br(C₆F₅)(p-C₆F₅CN)] (14c) and a disubstituted product [*o*-Br(C₆F₅)(p-C₆F₅ CN)₂] (15c) at relatively low yields (6% for 14c and 5% for 15c, Table 3, entry 11). Similar to 1a, the product 14c was produced by the coupling reaction between the C–F bond at the *para*-position of CN of 1c and the C–Si bond of *o*-Br(C₆F₅)SiMe₃, and successive coupling reactions occurred at the *para*-position of CN of 1c molecule with the C–Br bond in 14c. The route to the protonated monosubstituted product 17 is only seen in the reactions of *o*-Br(C₆F₅)SiMe₃ with 1b, but not with 1a and 1c. The formation of 15 is also possible through the intermediate 16, and if so, the intermediate 16 bifurcated only through 16b but not through 16a and 16c. If this is not the case, the route to 16 is only operative for 1b but not for 1a and 1c. It is not yet clear which of these synthesis routes can explain the observed results.
However, it is important to note that the C−Br bond participated in the Ar−Ar coupling as well as the C−Si bond under the experimental conditions. The products 15a, 15c, and 17b were totally unexpected, so we carefully examined their 19F NMR data by density functional theory (DFT) calculation to confirm their structures. The unexpected Ar−Ar coupling between C−Br and C−F bonds suggests further study, probably for developing a very new Ar−Ar coupling reaction without any metal catalyst. That work, however, is beyond the scope of this paper and will be the subject of a future study.

The structures of the perfluorinated arenes synthesized in this study were determined by 1H, 19F, and 13C NMR spectroscopies and gas chromatography−mass spectrometry (GC−MS). The NMR analyses gave valuable information for the identification of the perfluorinated arenes having several geometrical isomers. However, the signal of synthesized perfluorinated arenes was significantly shifted due to the conjugated π-electrons associated with the electron-withdrawing substituent; therefore, the assignments of NMR signals were also confirmed by DFT calculations. In our previous reports, when the DFT calculation was performed at the B3LYP level using the gauge-independent atomic orbital (GIAO) level with the 6-31++G(d,p) basis set, the chemical shift of poly- and perfluorinated compounds could be reproduced unerringly. The usefulness of DFT calculations for spectral assignments of 13C, 15N, and 19F NMR chemical shifts using the B3LYP-GIAO/6-31++G(d,p) level was further illustrated in Figure 2. Correlation between the experimentally determined and calculated 13C NMR chemical shifts is also given in the Supporting Information (Tables S9−S14).

The calculated 19F NMR shieldings showed reasonably good agreement with the experimentally determined values, although they tended to take slightly smaller values [Δδ(F) = −0.19 to −7.82]. Larger differences were observed for the CF3 groups [Δδ(F) = −9.12 to −10.00] (Tables S9−S11). Among the perfluoroaryl cyclic imines, the difference between calculated and experimental values in aliphatic fluorine was larger than that in aromatic fluorine.

According to the assignment of the 19F NMR signal, the most significant effect of the electron-withdrawing substituent appeared in the fluorine adjacent to the substituent [CN (ca. −145 ppm) < CF3 (ca. −139 ppm) < C6F5 (ca. −136 ppm) < NO2 (ca. −134 ppm)]. The 19F signal of the aromatic ring originating from C6F4(SiMe3)2 was slightly shifted by the electron-withdrawing substituent in the disubstituted product, while its chemical shift was changed by hydrogen and bromine atoms in the monosubstituted product. The site of the perfluorinated arene (para or ortho) attacked by the electron-withdrawing substituent could be easily determined by the signal patterns and chemical shifts of aromatic fluorine atoms, which were well reproduced by the DFT calculation.

In comparison with 19F NMR values, the calculated 13C NMR shieldings showed better agreement with experimentally determined values [Δδ(C) = −3.89 to 4.07], except for the signals of CF3, CN, and C-Br groups (Tables S12−S14). The differences between the calculated and measured values were smaller in aromatic carbons connected with fluorine (135−160 ppm) than those of aromatic carbons connected with another carbon ring (95−115 ppm). The CF3 and C-Br groups had similar calculated 13C NMR shieldings (124−128 ppm), which took on larger values than the experimentally determined values, as follows: CF3 [Δδ(C) = 6.18−7.14]; C-Br [Δδ(C) = 9.17−10.18]. Meanwhile, the CN group exhibited smaller calculated 13C NMR-shielding values (98−100 ppm) although the experimentally measured values for the CN group were larger than the corresponding calculated values [Δδ(C) = −6.47 to −8.19]. For the experimentally determined 13C NMR shieldings, the electron-withdrawing substituent significantly affected the carbon directly connected with it in the following order: CN (ca. 97 ppm) < CF3 (ca. 112 ppm) < NO2 (ca. 131 ppm) < C6F5 (ca. 144 ppm). The tendency of signal shifts due to the electron-withdrawing substituent gave beneficial

![Figure 1. Correlation between the experimentally determined and calculated 19F NMR shieldings.](image1)

![Figure 2. Correlation between the experimentally determined and calculated 13C NMR shieldings.](image2)
information for assigning signals to complicated perfluorinated arenes that were present as several geometrical isomers.

As described above, bifunctional perfluoroarylsilanes, C₆F₄(SiMe₃)ₓ, are useful reagents for manufacturing fluorine materials having not only bifunctional units but also various positional isomers on biphenyl and terphenyl skeletons. The electron-withdrawing substituents on these molecules can be easily converted to a reactive site for another bifunctional molecule having the terphenyl unit. The NMR analysis presented in this study can also apply to perfluorinated arenes having several aromatic rings, which may serve as fluorinated materials for industrial applications. In the future, we are planning to investigate synthesis and NMR analysis of fluorinated arenes having more complicated skeletons, from the point of view of the utilization of perfluorinated materials for a wide range of industrial fields.

■ CONCLUSIONS

Use of anhydrous CH₃CN at a low reaction temperature (−30 °C) produced 1,3-bis(trimethylsilyl)tetrafluorobenzene [m-C₆F₄(SiMe₃)₂] as well as 1,4-bis(trimethylsilyl)-tetrafluorobenzene [p-C₆F₄(SiMe₃)₂], from the corresponding dibromotetrafluorobenzene. This modified method to prepare a bifunctional trimethylsilyl-based transfer reagent could not be applied to the ortho-isomer; therefore, it only provided 1-bromo-2-trimethylsilyl-3,4,5,6-tetrafluorobenzene [o-Br(C₆F₄)(C₆F₄CF₃), SiMe₃] instead of the desired product, [o-(C₆F₄CF₃)(SiMe₃)]. In the reaction of perfluoroarenes (C₆F₄X) having an electron-negative substituent (CF₃, C₆F₅, CN, or NO₂) with both p-C₆F₄(SiMe₃) and m-C₆F₄(SiMe₃), the para-position of the electronegative substituent reacted with both the C–Si bonds to produce disubstituted perfluoroarenes [C₆F₄(p-C₆F₄X)]. This reaction proceeded via monosubstituted silylates [C₆F₄(SiMe₃)(p-C₆F₄X)], which were not isolable due to being unstable, and yielded protonated monosubstituted perfluoroarenes [HC₆F₄(p-C₆F₄X)]. In cases of the conjugated bond (CN and NO₂), the ortho-position was also attacked to produce positional isomers [C₆F₄(o-C₆F₄X)] and [HC₆F₄(o-C₆F₄X)] at even lower yields. Perfluoroarenes also reacted with o-Br(C₆F₄)SiMe₃ to provide monosubstituted bromide [o-Br(C₆F₄)(p-C₆F₄X)], along with unexpected Ar–Ar coupling products, such as the disubstituted product o-C₆F₄(p-C₆F₄X, X = SiMe₃), CN) and a protonated monosubstituted product 6′-H(C₆F₄)(p-C₆F₄X) (X = C₆F₅). The combination of experimentally determined and calculated NMR shieldings provided significant information for determining structures of complicated perfluorinated materials with several aromatic rings, which can be used in various industrial fields.

■ EXPERIMENTAL SECTION

General Remarks. The ¹H and ¹³C NMR spectra were measured on a Varian INOVA-300 spectrometer with CDCl₃ as the solvent operated at 299.95 and 75.42 MHz, respectively. The ¹³F NMR spectra were measured using the same solvent and spectrometer operated at 282.24 MHz; positive δ values were downfield from the internal reference, CFCl₃. The GC–MS data were obtained with a JEOL jms-kg/STK Ultra Quad GC/MS instrument, using electron-impact ionization at 70 eV. The TD-GC–MS data were obtained with a Shimadzu GCMS-QP2010 Ultra instrument, which used electron-impact ionization at 70 eV after the sample was sublimed from 100 to 600 °C. All solvents were purchased as superdehydrated solvents commercially and were used without further purification.

Preparation of 1,4-Bis(trimethylsilyl)tetrafluorobenzene [p-C₆F₄(SiMe₃)₂]. A solution of 1,4-dibromo-2,3,5,6-tetrafluorobenzene (2.00 g, 6.50 mmol) and chloro-trimethylsilane (1.48 g, 13.6 mmol) in 5 mL of anhydrous acetonitrile was placed in a 100 mL round-bottom flask with a three-way stopcock. The reaction mixture was stirred in a dry ice-ethanol bath at −50 °C, and tri(diethylamino)phosphate (3.38 g, 13.7 mmol) was added from a dropping funnel over 20 min. After stirring at −30 °C for 3 h, the reaction mixture became a yellow suspension. The white solid was collected by filtration of the cooled reaction mixture at −30 °C and then was washed twice with a small amount of the cooled anhydrous acetonitrile. After the white solid was dissolved in anhydrous acetonitrile under gentle heating at 50 °C, the solution was cooled at −30 °C to yield white crystals of 1,4-bis-(trimethylsilyl)tetrafluorobenzene [p-C₆F₄(SiMe₃)₂], with a mass of 1.14 g (3.86 mmol), a 59% yield. ¹H NMR (299.95 MHz, CDCl₃): δ 0.39 (SiMe₃), ¹³F NMR (282.22 MHz, CDCl₃): δ −129.31 (s, 2F, 3,5,6-F), ¹³C(¹H,¹³F) NMR (75.4 MHz, CDCl₃): δ 0.10 (SiMe₃), 118.54 (1,4-C), 148.69 (2,3,5,6-C); GC–MS (m/z, %): 294 [M⁺, 100%].

Reaction of Octafluorotoluene (1a) with p-C₆F₄(SiMe₃)₂. A solution of p-C₆F₄(CF₃) (90 mg, 0.306 mol) and a catalytic amount (10 mg) of KHF₂ in 2 mL of anhydrous DMF was placed in a 30 mL Teflon vessel, and then a solution of octafluorotoluene (1a) (146 mg, 0.618 mmol) with 1 mL of anhydrous DMF was added while gently stirring with a magnetic stirrer. After stirring at room temperature (RT) for 20 h, the reaction mixture turned to a light-yellow suspension. A white solid was collected from the suspension and was purified using Kugelrohr distillation to provide p-C₆F₄(CF₃) (3a) as white needles. On the other hand, a light-yellow solid was obtained by evaporation of the filtrate and was distilled by the Kugelrohr apparatus to produce 4′-H(C₆F₄)(p-C₆F₄CF₃) (3a) as the lower-temperature fraction and p-C₆F₄(CF₃)(p-C₆F₄CF₃) (4a) as the higher-temperature fraction. The yield of 3a isolated from the Kugelrohr distillate was 2%, while that of 4a was 34%, isolated from the Kugelrohr distillates of both the precipitate and filtrate.

4′-Perfluoro(4-methyl-1,1′-biphenyl) (3a). Yield: 2% (isolated yield for the Kugelrohr distillate); ¹H NMR (299.95 MHz, CDCl₃): δ 7.14 (m, 4′-H); ¹³F NMR (282.22 MHz, CDCl₃): δ −56.92 (6F, t, J = 21.87 Hz, CF₃), −135.97 (2F, m, 2.6-F), −137.36 (2F, m, 2.6′-F), −138.24 (2F, m, 3-F), −139.56 (2F, m, 3′,5′-F); ¹³C(¹H,¹³F) NMR (75.42 MHz, CDCl₃); δ 106.01 (1′-C), 108.77 (4′-C), 111.55 (4-C), 117.19 (1-C), 120.48 (CF₃), 143.87 (2′,6′-C), 144.18 (2,6-C), 144.31 (3,5-C), 146.16 (3′,5′-C); GC–MS (m/z, %): 366 [M⁺, 100%], 347 [M⁺−F, 45%], 316 [M⁺−CF₃, 84%], 297 [M⁺−CF₃, 15%], 278 [M⁺−F−CF₃, 27%], 247 [M⁺−F−CF₃, 22%], 234 [M⁺−H−CF₃, 44%].

Perfluoro(4,4′-dimethyl-1,1′-terphenyl) (4a). Yield: 34% (isolated yield for the Kugelrohr distillates from both precipitate and filtrate); ¹³F NMR (282.22 MHz, CDCl₃): δ −56.97 (6F, t, J = 10.7 Hz, CF₃), −135.46 (4F, m, 2.6-F and 2′,6′-F), −136.18 (4F, m, 2′,3′,5′,6′-F), −138.92 (4F, m, 3′,5′-F and 3′,5′-F); ¹³C(¹H,¹³F) NMR (75.42 MHz, CDCl₃); δ 108.82 (1′-C), 110.73 (1″-C), 112.24 (4′-C), 120.53 (CF₃), 144.22 (2′,3′,5′,6′-C), 144.45 (3,5-C and 3′,5′-C), 144.49 (2,6-C and 2′,6′-C); GC–MS (m/z, %): 582 [M⁺,
100], 563 [M′−F, 22], 532 [M′−CF3, 20], 513 [M′−CF3, 5], 494 [M′−F−CF3, 8], 463 [M′−C3F7]

Reaction of Decafluoro-1,1′-biphenyl (1b) with p-C6F5(SiMe3)3. A solution of p-C6F5(SiMe3)3 (90 mg, 0.306 mmol) and 11 mg of KHF2 in 2 mL of anhydrous DMF was placed in a 30 mL Teflon vessel, and then a solution of decafluorobiphenyl 1b (205 mg, 0.613 mmol) with 1 mL of anhydrous DMF was added while gently stirring. After stirring at RT for 60 h, the reaction mixture became a white suspension. A white solid was collected by filtration of the light-yellow suspension and was purified using Kugelrohr distillation to provide p-C6F5(p-C6F5C6F5)2 (4b) as a white solid. A light-yellow solid was obtained by evaporation of the filtrate and was distilled with the Kugelrohr apparatus to provide 4′-H(C6F5)2(p-C6F5C6F5)2 (3b) as a white solid.

4′H-Perfluoro(1,1′,4,1′-terphenyl) (3b). Yield: 2% (determined by 19F NMR for the Kugelrohr distillates); 1H NMR (299.95 MHz, CDCl3): δ 7.31 (4′-H). 19F NMR (282.2 MHz, CDCl3): δ −137.16 (2F, m, 2,6-F), −136.98 (2F, m, 2,6′-F), −136.97 (2F, m, 2,6′-F); 13C(F3) NMR (75.42 MHz, CDCl3): δ 96.22 (4-C), 106.34 (CN), 106.89 (1′-C), 109.13 (4′-C), 114.61 (1-C), 143.79 (2,6-C), 144.20 (2′,6′-C), 146.17 (3,5′-C), 147.29 (3,5-C); GC−MS (m/z, %): 323 [M′+, 100], 304 [M′−F, 9], 285 [M′−2F, 15], 254 [M′−CF3, 91].

4′H-Perfluoro(1,1′-biphenyl-2-carbonitrile) (6c). Yield: below 1% (determined by 19F NMR of the Kugelrohr distillates); 1H NMR (299.95 MHz, CDCl3): δ 7.31 (4′-H). 19F NMR (282.2 MHz, CDCl3): δ −138.66 (1F, m, 4-F), −132.38 (1F, m, 6-F), −138.73 (2F, m, 2′,6′-C), −143.02 (1F, m, 5-F), −148.60 (1F, m, 3-F); GC−MS (m/z, %): 323 [M′+, 100], 254 [M′−CF3, 13].

Perfluoro(1,1′,4,1′-terphenyl-4,4′-dicarbonitrile) (4c). Yield: 39% (isolated yield for the Kugel Rohr distillate); 19F NMR (282.2 MHz, CDCl3): δ −130.64 (4F, m, 3,5,3′,5′-F); −134.09 (4F, br s, 2,6-F and 2,6′-F), −135.52 (4F, m, 2,3′,5′,6′-F); 13C(F3) NMR (75.42 MHz, CDCl3): δ 96.95 (4,4′-C), 106.73 (CN), 108.81 (1-C and 1′-C), 112.57 (1′-C), 144.14 (2,3′,5′-C), 144.16 (2′,6′-C and 2,6′-C), 147.39 (3,5-C and 3,5′-C); GC−MS (m/z, %): 496 [M′+, 100], 427 [M′−CF3, 18].

Perfluoro(1,1′,4,1′-terphenyl-2,4′-dicarbonitrile) (7c). Yield: below 1% (determined by 19F NMR of the Kugel Rohr distillates); 19F NMR (282.2 MHz, CDCl3): δ −127.72 (1F, m, 3-F), −130.83 (2F, m, 2′,6′-F), −131.68 (1F, m, 6-F), −133.57 (2F, m, 3,5′-F), −135.17 (2F, m, 3′,5′-F), −136.24 (2F, m, 2′,6′-F), −142.19 (1F, m, 5-F), −147.20 (1F, m, 4-F); GC−MS (m/z, %): 496 [M′+, 100], 427 [M′−CF3, 12].

Reaction of Pentafluoronitrobenzene (1d) with p-C6F5(SiMe3)3. A solution of p-C6F5(SiMe3)3 (90 mg, 0.306 mmol) and 10 mg of KHF2 in 2 mL of anhydrous DMF was placed in a 30 mL Teflon vessel, and a solution of pentafluoronitrobenzene 1d (133 mg, 0.624 mmol) in 1 mL of anhydrous DMF was added while gently stirring. After reaction at RT for 20 h, the mixture turned to an orange solution. The mixture was evaporated to give an orange oil, which was distilled using the Kugelrohr apparatus. The first fraction provided a mixture of 4′-H(C6F5)2(p-C6F5NO2) (3d) and a small amount of its positional isomer, 4′-H(C6F5)2(o-C6F5NO2) (6d), while the second fraction yielded 3d in the pure form. The third fraction consisted of p-C6F5(C6F5NO2)2 (4d) with a small amount of its isomer, p-C6F5(o-C6F5NO2)(p-C6F5NO2) (7d); however, 4d could not be isolated in the pure form.

4′H-Perfluoro(4-nitro-1,1′-biphenyl) (3d). Yield: 8% (isolated yield for the Kugel Rohr distillate); 1H NMR (299.95 MHz, CDCl3): δ 7.34 (m, 4′-H). 19F NMR (282.2 MHz, CDCl3): δ −133.91 (2F, m, 2,6-F), −136.96 (2F, m, 2,6′-F), −138.00 (2F, m, 3,5′-F), −145.74 (2F, m, 3,5′-F); 13C(F3) NMR (75.42 MHz, CDCl3): δ 106.05 (1′-C), 109.14 (4′-C), 111.34 (1-C), 131.49 (4-C), 140.26 (3,5-C), 143.83 (2,6-C), 144.37 (2′,6′-C), 146.19 (3,5′-C); GC−MS (m/z, %): 343 [M′+, 100], 327 [M′−O, 10], 313 [M′−NO2, 19], 297 [M′−NO2−NO2, 14], 285 [M′−CNO2−O, 12], 278 [M′−NO−F, 37], 247 [M′−NO2−CF3, 30].

4′H-Perfluoro(2-nitro-1,1′-biphenyl) (6d). Yield: determined by 19F NMR for the Kugel Rohr distillates); 1H NMR (299.95 MHz, CDCl3): δ 7.28 (m, 4′-H). 19F NMR (282.2 MHz, CDCl3): δ −133.05 (1F, m, 6-F), −137.07 (2F, m, 2′,6′-F), −139.21 (2F, m, 3,5′-F), −143.12 (1F, m, 4-F), −146.24 (1F, m, 5-F), −147.32 (1F, m, 3-F); GC−MS (m/z,
**:1**-Flouro-$4,4'$-dinitro-$1,1'$-terphenyl (9a). Yield: 4% (isolated yield for the Kugelrohr distillates); **1**H NMR (299.95 MHz, CDCl$_3$): δ 7.00 (m, 5H); **19**F NMR (282.2 MHz, CDCl$_3$): δ −56.92 (6F, t, J = 22.44 Hz, C$_F_2$), −113.28 (1F, m, 6F), −127.01 (1F, m, 2F), −130.07 (1F, m, 4F), −136.22 (2F, m, 2F), −139.87 (2F, m, 3F, 5F), −163.23 (1F, m, 3F, 5F); **13**C($^1$H,$^19$F) NMR (75.42 MHz, CDCl$_3$): δ 101.18 (1′-C), 101.79 (5′-C), 111.26 (1′-C), 111.79 (4′-C), 120.59 (C$_F_2$), 137.65 (3′-C), 144.26 (3,5-C), 144.56 (2′-C), 149.17 (2′-C), 152.54 (4′-C), 154.50 (6′-C); GC–MS (m/z %): 366 [M+H]$,^+$, 300; 316 [M−C$_F_2$], 297 [M−C$_F_2$, 13], 278 [M−F−C$_F_3$, 31], 247 [M−F−C$_{19}$F$_3$, 30].

**Perfluoro(4,4''-Dimethyl-1,1''3,1'-terphenyl) (10a).** Yield: 35% (isolated yield for the Kugelrohr distillates); **1**H NMR (282.2 MHz, CDCl$_3$): δ −56.94 (6F, t, J = 23.42 Hz, C$_F_2$), −112.06 (1F, m, 2F), −125.32 (2F, m, 4F, 6F), −135.76 (4F, m, 2F and 2′,6F), −139.19 (4F, m, 3F and 3′,5F), −160.44 (1F, m, 5F); **13**C($^1$H,$^19$F) NMR (75.42 MHz, CDCl$_3$): δ 102.08 (1′,3′-C), 110.08 (1′-C and 1′-C), 111.88 (4′-C and 4′-C), 120.52 (C$_F_2$), 138.05 (5′-C), 144.38 (3,5-C and 3′,5′-C), 144.56 (2′-C and 2′′-C), 150.37 (4′,6′-C), 152.09 (2′-C); GC–MS (m/z %): 582 [M$^+$, 100], 563 [M$^+$−F, 24], 532 [M$^+$−C$_F_2$, 20], 513 [M$^+$−C$_{19}$F$_3$, 7], 494 [M$^+$−F−C$_{19}$F$_3$, 7].

**Reaction of Decafluoro-$1,1'$-biphenyl (1b) with $m$-C$_6$F$_4$($^3$SiMe$_3$)$_2$ ($p$-C$_6$F$_4$($^3$SiMe$_3$)$_2$) (9a) as a white solid, and the higher-temperature fraction provided $m$-C$_6$F$_4$($^3$SiMe$_3$)$_2$($p$-C$_6$F$_4$($^3$SiMe$_3$)$_2$) (10b), also a white solid.

**5'H-Perfluoro-(4-methyl-1,1'-biphenyl) (9a).** Yield: 4% (isolated yield for the Kugelrohr distillates); **1**H NMR (299.95 MHz, CDCl$_3$): δ 7.00 (m, 5H); **19**F NMR (282.2 MHz, CDCl$_3$): δ −56.92 (6F, t, J = 22.44 Hz, C$_F_2$), −113.28 (1F, m, 6F), −127.01 (1F, m, 2F), −130.07 (1F, m, 4F), −136.22 (2F, m, 2F), −139.87 (2F, m, 3F, 5F), −163.23 (1F, m, 3F, 5F); **13**C($^1$H,$^19$F) NMR (75.42 MHz, CDCl$_3$): δ 101.18 (1′-C), 101.79 (5′-C), 111.26 (1′-C), 111.79 (4′-C), 120.59 (C$_F_2$), 137.65 (3′-C), 144.26 (3,5-C), 144.56 (2′-C), 149.17 (2′-C), 152.54 (4′-C), 154.50 (6′-C); GC–MS (m/z %): 366 [M$^+$, 100], 316 [M$^+$−C$_F_2$], 297 [M$^+$−C$_F_2$, 13], 278 [M$^+$−F−C$_F_2$, 31], 247 [M$^+$−F−C$_{19}$F$_3$, 30].
Reactivity of Pentafluorobenzonitrile (1c) with m-C6F4(SiMe3)2. A solution of m-C6F4(SiMe3)2 (178 mg, 0.61 mmol) and 10 mg of KH[F2] in 2 mL of anhydrous DMF was placed in a 30 mL Teflon vessel. A solution of pentafluorobenzonitrile 1c (232 mg, 1.20 mmol) in 1 mL of anhydrous DMF was added while stirring. After 20 h of RT reaction, the mixture became an orange solution. The solution was evaporated to yield a brown oil, which was distilled with the Kugelrohr apparatus. The first fraction provided a mixture of 5′-[H(C6F4)(p-C6F4NO2)] (9d) and a small amount of its positional isomer, 5′-[H(C6F4)(o-C6F4NO2)] (12d). The second fraction consisted of m-C6F4(p-C6F4NO2) (10d) with a small amount of its isomer, m-C6F4(o-C6F4NO2)(p-C6F4NO2) (13d). Both the mono- and bis-C6F4NO2 substituted products 9d and 10d could not be obtained in the pure form because these positional isomers (12d and 13d) could not be separated by distillation.

5′-Perfluoro-(4-nitro-1,1′-biphenyl-4-carbonitrile) (9c). Yield: 25% (determined by 19F NMR for the Kugelrohr distillate); 1H NMR (299.95 MHz, CDCl3): δ 7.03 (m, 3′-H); 19F NMR (282.2 MHz, CDCl3): δ −113.05 (1F, m, 6′-F), −126.17 (1F, m, 4′-F), −129.83 (1F, m, 2′-F), −134.15 (2F, m, 2,6-F), −145.99 (2F, m, 3,5-F), −162.79 (1F, m, 3′-F); 13C{1H,19F} NMR (75.42 MHz, CDCl3): δ 100.59 (5-C), 101.96 (1′-C), 111.55 (1-C), 131.26 (4-C), 137.70 (3′-C), 140.24 (3,5-C), 144.43 (2,6-C), 149.15 (2′-C), 152.77 (6′-C), 154.48 (4′-C); GC–MS (m/z, %): 343 [M′+, 100], 313 [M′−NO, 19], 297 [M′−NO2, 18], 285 [M′−CNO2, 38], 278 [M′−NO2−F, 57], 247 [M′−NO2−CF3, 51].

5′-Perfluoro-(2-nitro-1,1′-biphenyl) (12d). Yield: 6% (determined by 19F NMR for the Kugelrohr distillate); 1H NMR (299.95 MHz, CDCl3): δ 7.04 (m, 4′-H); 19F NMR (282.2 MHz, CDCl3): δ −114.48 (1F, m, 6′-F), −126.71 (1F, m, 4′-F), −130.94 (1F, m, 2′-F), −143.18 (1F, m, 3-F), −143.53 (1F, m, 6-F), −146.58 (2F, m, 3-F), −147.86 (1F, m, 4-F), −162.83 (1F, m, 3′-F); GC–MS (m/z, %): 343 [M′+, 100], 297 [M′−NO2, 14], 278 [M′−NO2−F, 26], 247 [M′−NO2−CF3, 35].

Perfluoro(4,4′-dinitro-1,1′-3,1′-terphenyl) (10d). Yield: 16% (determined by 19F NMR for the Kugelrohr distillate); 1F NMR (282.2 MHz, CDCl3): δ −117.12 (1F, m, 2′-F), −124.38 (2F, m, 4′,6′-F), −133.69 (4F, m, 2,6′-F and 2′,6′-F), −145.28 (4F, m, 3,5-F and 3,5′-F), −159.62 (1F, m, 5′-F); 13C{1H,19F} NMR (75.42 MHz, CDCl3): δ 101.64 (1′-C), 110.38 (1-C and 1′-C), 131.71 (4-C and 4′-C), 138.15 (5′-C), 140.34 (3,5-C and 3,5′-C), 144.45 (2,6-C and 2′,6′-C), 150.57 (4′-C), 152.07 (2-C); GC–MS (m/z, %): 536 [M′+, 100], 520 [M′−O, 7], 506 [M′−NO2, 27], 478 [M′−CNO2−11, 460 [M′−4F, 23], 444 [M′−2NO2, 34], 432 [M′−O−CF3, 24], 425 [M′−2NO2−F, 18], 406 [M′−2NO2−2F, 25], 375 [M′−2NO2−CF3, 31].

Perfluoro(2,4′-dinitro-1,1′-3,1′-terphenyl) (13d). Yield: 9% (determined by 19F NMR for the Kugelrohr distillate); 1F NMR (282.2 MHz, CDCl3): δ −113.06 (1F, m, 2′-F), −124.96 (1F, m, 6′-F), −125.68 (1F, m, 4′-F), −132.72 (1F, m, 6-F), −133.25 (1F, m, 3-F), −133.92 (2F, m, 2′,6′-F), −142.38 (1F, m, 4-F), −145.56 (2F, m, 3,5′-F), −146.38 (1F, m, 5′-F), −159.63 (1F, m, 5′-F); GC–MS (m/z, %): 536 [M′+, 100], 520 [M′−O, 23], 506 [M′−NO2, 10], 490 [M′−NO2−27].

Reaction of 1,2-Dibromo-3,4,5,6-tetrafluorobenzene with Chlorotrimethylsilane. A solution of 1,2-dibromo-3,4,5,6-tetrafluorobenzene (2.89 g, 9.39 mmol) and chlorotrimethylsilane (2.04 g, 18.7 mmol) in 5 mL of anhydrous acetonitrile was placed in a 100 mL round-bottom flask with a three-way stopcock. The reaction mixture was stirred at −30 °C, and tri(isoamylamine)phosphate (4.64 g, 18.8 mmol) was added dropwise over 10 min. After stirring at −30 °C for 3 h, the mixture was allowed to warm to room temperature, and the reaction mixture was concentrated in vacuo to 5 mL.

The product was purified by column chromatography on silica gel with gradient elution (10% to 20% Me2CO in CH2Cl2) to give a white solid in an 44% yield (0.814 g).
the reaction mixture became a light-yellow suspension. The reaction temperature was maintained for 6 h, after which the liquid phase was removed from the mixture by decantation. The residual white solid turned into a two-layer liquid after being brought to room temperature. The lower layer was collected and distilled under vacuum. The resulting clear liquid was 1-bromo-2-trimethylsilyl-3,4,5,6-tetramethylbenzene [o-Br-(C6H4)2SiMe3]. A yield of 0.705 g (2.39 mmol, a 25% yield) was obtained at 77–78 °C at 10 mmHg including 16 wt % of O=P(NEt3)2. 19F NMR (299.95 MHz, CDCl3): δ = 0.47 (d, J = 2.4 Hz, 2-SiMe3). 13C{1H,19F} NMR (75.4 MHz, CDCl3): δ = 123.63 (1F, m, 3-F), 149.81 (1F, m, 4-F), 143.11 (1F, m, 5-F). 13C{1H} NMR (75.4 MHz, CDCl3): δ = 113.83 (1-C and 1′-C), 142.52 (4,6-,6′-F). The reaction mixture was evaporated, yielding a yellow oil, which was Kugelrohr distilled. The first fraction consisted of o-Br(C6F4)2SiMe3 (268 mg, 0.89 mmol) and 0.20 mmol O=P(NEt3)2, an impurity that was placed in a 30 mL Teflon vessel along with 2 mL of anhydrous DMF and a catalytic amount (12 mg) of KHF. To this mixture was added 377 mg (1.60 mmol) of octafluorotoluene 1a in 1 mL of anhydrous DMF. After stirring at RT for 20 h, the mixture became an orange solution. The mixture was evaporated, and a reaction solution. The solution was evaporated to give a yellow solid. A mixture of o-Br(C6F4)2(p-C6F4(C2F5)F) (14b) and 6′-H(C6F4)(p-C6F4(C2F5)F) (17b) was obtained by sublimation of the solid and using the Kugelrohr distillation apparatus. Although these substituted perfluoroterephthyl products could not be separated, their structures were determined in the mixed form.

Perfluoro(2-bromo-1,′,2,″-terphenyl) (14b). Yield: 10% (determined by 19F NMR for the Kugelrohr distillates); 19F NMR (282.2 MHz, CDCl3): δ = −126.88 (1F, ddd, J = 21.5, 9.6, 4.0 Hz, 3-F), −133.78 (1F, m, 6-F), −137.29 (2F, m, 2′,6′-F), −137.34 (2F, m, 2′,6′-F), −137.56 (2F, m, 3′,5′-F), −139.46 (1F, m, 4′-F), −149.81 (1F, m, 5-F), −154.04 (1F, m, 5-F), −160.62 (2F, m, 3′,5′-F); GC–MS (m/z, %): 542 [M′ + 100], 496 (44), 427 (24), 463 [M′−Br − C2F5], 413 [M′−Br−CF3], 375 [M′−Br−F−CF2], 28, 344 [M′−Br−C2F5].

6′-H-Perfluoro(1,′,2,″-terphenyl) (17b). Yield: 8% (determined by 19F NMR for the Kugelrohr distillates); 1H NMR (299.95 MHz, CDCl3): δ = 7.11 (m, 6′-H); 19F NMR (282.2 MHz, CDCl3): δ = −136.51 (1F, m, 2′-F), −137.37 (2F, m, 2′,6′-F), −138.20 (1F, m, 5′-F), −139.56 (2F, m, 3′,5′-F), −149.89 (1F, m, 4′-F), −151.78 (1F, m, 4′-F), −153.73 (1F, m, 3′-F), −160.54 (2F, m, 3′,5′-F); GC–MS (m/z, %): 464 [M′ + 100], 395 [M′−Br−C2F5], 364 [M′−C2F5].

Reaction of Pentatfluorobenzonitrile (1c) with o-Br(C6F4)2SiMe3. A mixture of o-Br(C6F4)2SiMe3 (268 mg, 0.89 mmol) and 0.20 mmol O=P(NEt3)2 was placed in a 30 mL Teflon vessel into which 2 mL of anhydrous DMF and 12 mg of KHF were added. When a solution of pentatfluorobenzonitrile 1c (311 mg, 1.61 mmol) in 1 mL of anhydrous DMF was added to the mixture under stirring, the reaction mixture turned deep-brown immediately. The reaction mixture was still a deep-brown solution after 20 h of stirring. The mixture was evaporated to give a dark-brown oil, which was Kugelrohr distilled to yield a first fraction of o-Br(C6F4)2(p-C6F4(CN)2) (14c) as a yellow liquid accompanied by O=P(NEt3)2. An orange oil with white crystals was obtained as the second distillation fraction, from which o-Br(C6F4)(p-C6F4(CN)2) (15c) was obtained as white needles by washing with a small amount of CHCl3.

Perfluoro(2′-bromo-1,′,2-′-biphenyl-4-carbonitrile) (14c). Yield: 6% (determined by GC for the Kugelrohr distillates); 19F NMR (282.2 MHz, CDCl3): δ = −126.26 (1F, m, 3′-F), −131.14 (1F, m, 6′-F), −133.61 (2F, m, 3′,5′-F), −134.78 (2F, m, 2′,6′-F), −145.04 (1F, m, 4′-F), −151.29 (1F, m, 5′-F); 13C{1H} NMR (75.4 MHz, CDCl3): δ = 96.43 (4-C), 106.68 (CN), 112.51 (1-C), 112.85 (1′-C), 117.55 (2′-C), 140.39 (5′-C), 142.49 (4′-C), 144.11 (2′,6′-C), 145.71 (6′-C), 146.32 (3′-C), 147.37 (3,5-C); GC–MS (m/z, %): 401 [M′, 100], 322 [M′−Br−C2F5, 303 [M′−Br−F−CF2, 84], 272 [M′−Br−CF3, 73], 253 [M′−Br−CF2].

Perfluoro(1,′,2,″-terphenyl-4,″-biscarbonitrile) (15c). Yield: 5% (isolated yield for the Kugelrohr distillate); 19F NMR (282.2 MHz, CDCl3): δ = −129.76 (4F, m, 3′,5′-F), −133.32 (2F, m, 3′,6′-F), −135.92 (4F, m, 2′,6′-F), −147.56 (2F, m, 4′,5′-F); 13C{1H} NMR (75.4 MHz, CDCl3): δ = 96.99 (4-C and 4′-C), 106.46 (4-CN and 4′-CN), 111.22 (1-C and 1′-C), 115.63 (1′-C), 142.52 (2′,6′-C), 143.88 (2′,6′-C), 145.93 (3′,5′-C), 147.11 (3,5-C and 3′,5′-C); GC–MS (m/z, %): 496 [M′ + 100], 477 [M′−
NMR but using Me₄Si (δref = 191.8000 ppm) as a reference.

Computational Method. Density functional theory (DFT) calculations were performed using the Gaussian 09 program package. All geometries were optimized at the B3LYP hybrid functional with the 6-31G(d,p) basis set. Calculations of vibrational frequencies were performed at the same level of theory to confirm minimum. Isotropic NMR-shielding tensors were calculated at the B3LYP level using the gauche-independent atomic orbital (GIAO) method with the 6-31+G(d,p) basis set. The 19F NMR shifts δ were calculated from the shielding (σ) as δ = σref − σ, where σref is the shielding of CFCl3 (σref = 179.3792 ppm). The calculated 13C NMR shifts were derived in the same fashion as the 19F NMR but using Me₄Si (σref = 191.8000 ppm) as a reference.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.9b03273. Cartesian coordinates with total energy (Tables S1–S8); experimentally determined and calculated values of NMR chemical shifts (Tables S9–S14) (PDF)

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Notes
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