Multiple Pentafluorophenylation of 2,2,3,3,5,6,6-Heptafluoro-3,6-dihydro-2*H*-1,4-oxazine with an Organosilicon Reagent: NMR and DFT Structural Analysis of Oligo(perfluoroaryl) Compounds

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The reagent $Me_3Si(C_6F_5)$ was used for the preparation of a series of perfluorinated, pentafluorophenyl-substituted 3,6-dihydro-2*H*-1,4-oxazines (**2**–**8**), which, otherwise, would be very difficult to synthesize. Multiple pentafluorophenylation occurred not only on the heterocyclic ring of the starting compound **1** (*Scheme*), but also in *para* position of the introduced C_6F_5 substituent(s) leading to compounds with one to three nonafluorobiphenyl ($C_{12}F_9$) substituents. While the tris(pentafluorophenyl)-substituted compound **3** could be isolated as the sole product by stoichiometric control of the reagent, the higher-substituted compounds **5**–**8** could only be obtained as mixtures. The structures of the oligo(perfluoroaryl) compounds were confirmed by ^{19}F- and ^{13}C-NMR, MS, and/or X-ray crystallography. DFT simulations of the ^{19}F- and ^{13}C-NMR chemical shifts were performed at the B3LYP-GIAO/6-31++G(d,p) level for geometries optimized by the B3LYP/6-31G(d) level, a technique that proved to be very useful to accomplish full NMR assignment of these complex products.

Introduction. – Perfluorinated compounds are being used as a wide variety of engineering polymers and surfactants on an industrial scale because of their unique thermal and chemical properties. Especially, perfluoroaryl compounds show several unique properties such as high electron affinity or a rather sterically demanding and π-electron-accepting nature compared with the corresponding non-fluorinated aryl systems. Several reports showed that strong *Lewis* acidity of a perfluoroaryl ring is efficient for catalytic reactions: perfluoroarylboranes as co-catalyst for the olefin polymerization with group-4 metallocene alkyls [1], bifunctional perfluoroarylboranes for the activation of basic substrates, and the selective binding of anions [2]. For the purpose of application of asymmetric catalysis, chiral bidentate (perfluoroaryl)phosphane ligands were synthesized [3]. Polymers containing perfluorophenylene moieties at the main chain are expected to be used in high-performance thermoplastics [4–6] and optical-waveguide devices [7][8]. Recently, tetrakis(pentafluorophenyl)porphyrin was reported to be applicable in various fields: imine aziridination [9], hydrogen peroxide induced oxidation [10], phenylethyne-linked porphyrin dyads [11], and as matrices for matrix-assisted laser-desorption-ionization (MALDI) mass spectrometry [12].

Fluorinated organosilicon compounds have been used as transfer reagents of fluorinated substituents for preparing synthetic intermediates in the areas of agrochemicals, pharmaceuticals, *etc.* [13]. Trimethyl(trifluoromethyl)silane, Me_3SiCF_3, is the most effective transfer reagent of a CF_3 moiety for various organic molecules, especially aldehydes and ketones [14]. A recent report has described the trifluoromethylation of less-reactive carboxylates, thiocyanates, and selenocyanates [15]. An aromatic analogue, $Me_3Si(C_6F_5)$, was also prepared by reaction of C_6F_5Br, Me_3SiCl, and $(Me_2N)_3P$ [16], and several reports were published on the pentafluorophenylation of organic molecules by $Me_3Si(C_6F_5)$, *e.g.*, perfluoro-olefins [17], perfluoro-aza-alkenes [18][19], or perfluorinated carbonyl compounds [20].

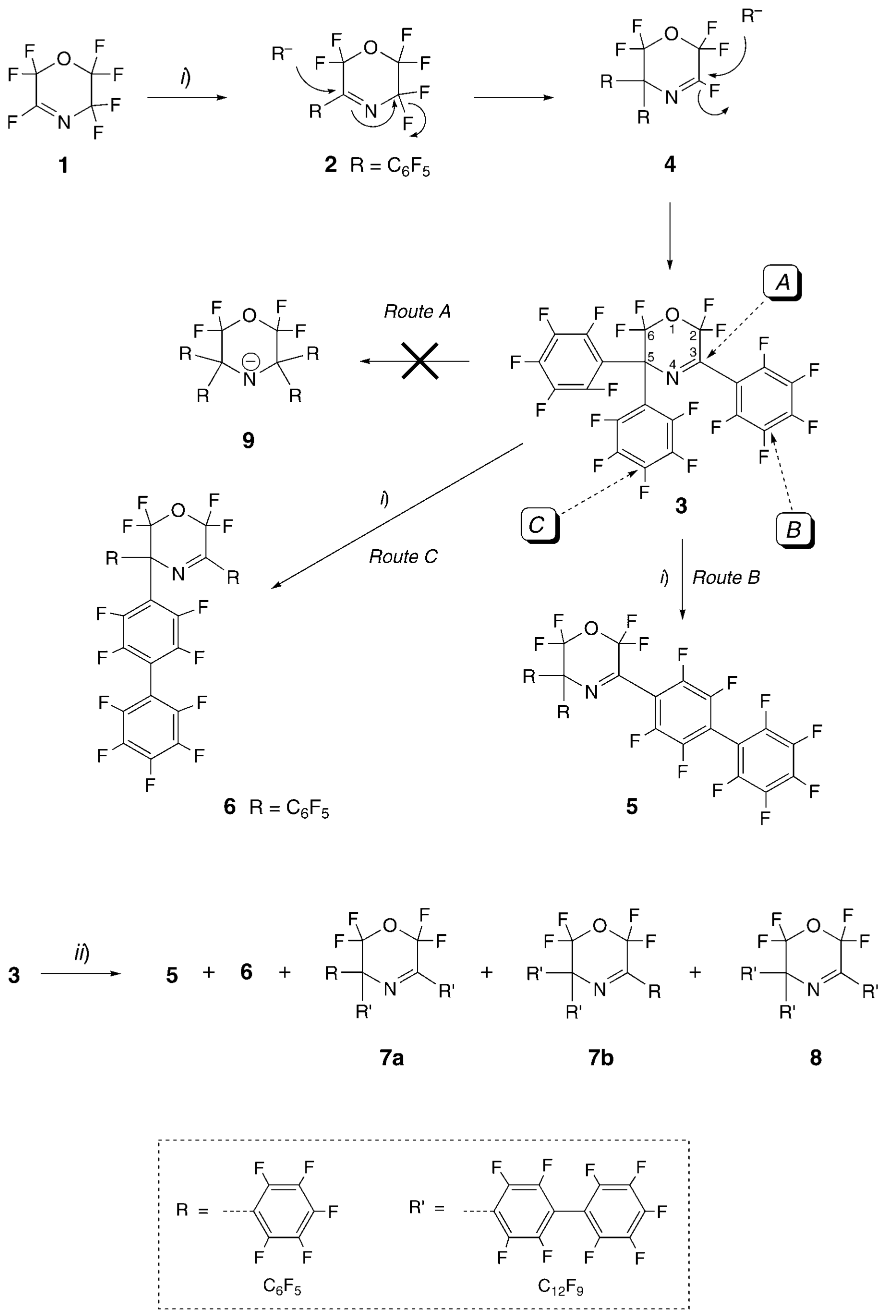
In a preliminary note [21], we described the reactions of $Me_3Si(C_6F_5)$ with highly electronegative and bulky substrates, focusing on a different reactivity between perfluorinated 3,4-dihydro-2*H*-pyrrole and perfluorinated 3,6-dihydro-2*H*-1,4-oxazine (**1**; see the *Scheme* below). This former study indicated that in the reaction of $Me_3Si(C_6F_5)$ the pyrrole predominantly provides dimerized products, while the reaction of the oxazine **1** affords C_6F_5-substituted derivatives without dimerization [21]. In the substitution reaction of perfluorinated *aliphatic* imines, such as perfluoro-aza-alkenes, oligomerization competes and a complex mixture is obtained. Differing from such perfluorinated imine systems, the suppression of the competing dimerization or oligomerization reaction found in the six-membered compound **1** prompted us to investigate in detail multiple pentafluorophenylations with $Me_3Si(C_6F_5)$, which led to a series of interesting perfluorinated products (*Scheme*) characterized spectroscopically and, in part, also by density-functional-theory (DFT) calculations.

Results and Discussion. – 1. *Synthesis.* Our approach towards the synthesis of new oligo- and poly(perfluoroaryl) materials was based on the reactions of compounds **1**–**3** with $Me_3Si(C_6F_5)$ under various conditions (*Scheme*). Because spray-dried KF, used as catalyst, is sensitive to moisture, all reactions with $Me_3Si(C_6F_5)$ were performed under anhydrous conditions in an inert atmosphere. Although the reactions proceeded well in MeCN, tetraglyme, and other aprotic polar solvents, MeCN was the solvent of choice since it allowed convenient product separation. The reactions were typically started at 0° for 1 h, and then run at ambient temperature for 20 h. The results are summarized in *Table 1*.

When equimolar amounts of $Me_3Si(C_6F_5)$ and **1** were used (*Table 1*, *Entry 1*), the mono-substituted compound **2** was obtained as the main product, accompanied by small amounts of the bis-adduct **4** and the tris-adduct **3**. When an excess of $Me_3Si(C_6F_5)$ was used, compound **3** was obtained in moderate-to-good yield, while **4** was still isolated in low yield (*Entries 2* and *3*). To attempt selective preparations of compounds **3** and **4**, reaction of the isolated mono-adduct **2** with $Me_3Si(C_6F_5)$ was next examined. When used in equimolar amounts (*Entry 4*), compound **4** was obtained in somewhat higher yield (16%; 28% based on consumed **2**). However, adduct **3** was present in the mixture in almost the same proportion (24%; 42% based on consumed **2**). Fortunately, the tris-adduct **3** was obtained as the sole product in 78% yield when using an excess of the reagent (*Entry 5*).

The pentafluorophenylation by $Me_3Si(C_6F_5)$ is considered to proceed *via* an addition–elimination mechanism (Ad_N-E): attack of $(C_6F_5)^-$ at the C=N bond and successive elimination of F^-. This mechanism works only when the C-atoms are directly bonded to the N-atoms so that the nucleophiles are only introduced into the neighbor-

Scheme



i) $Me_3Si(C_6F_5)$, KF (cat.), MeCN, 1 h at 0°, then 20 h at r.t. *ii*) $Me_3Si(C_6F_5)$, KF (cat.), MeCN, 1 h at 0°, then 48 h at 50°.

Table 1. *Reactions of* **1**–**3** *with* $Me_3Si(C_6F_5)$. Conditions: at 0° for 1 h, then at r.t. for 20 h, unless noted otherwise.

Entry	Compound ([mmol])	$Me_3Si(C_6F_5)$ [mmol]	KF [mmol]	Products[a])
1	**1** (3.3)	3.3	0.75	**2** (41), **3** (7.0), **4** (6.4)
2	**1** (1.1)	2.3	0.21	**2** (29), **3** (52), **4** (3.3)
3	**1** (3.2)	9.7	0.64	**2** (7.5), **3** (64)
4	**2** (0.44)	0.44	0.085	**2** (43), **3** (24), **4** (16)
5	**2** (0.41)	0.82	0.085	**2** (4.0), **3** (78)
6	**3** (0.30)	0.30	0.11	**3** (72), **5** (4.5), **6** (3.3)
7[b])	**3** (0.30)	0.97	0.11	**3** (5.6), **5** (8.3), **6** (3.5), **7a** (7.8), **7b** (3.0), **8** (0.6)[c])

[a]) Yields are given in % (in parentheses) and were determined by ^{19}F-NMR integration. [b]) At 50° for 48 h.
[c]) Together with a series of dimerization products (see *Fig. 2* and text).

ing C-atoms which is in contrast with the Ad_N-*E* reaction of perfluoro-olefin C=C systems, where multiple substitutions by nucleophiles around the perfluorocarbon skeletons are observed due to the migration of the C=C bonds, which leads to complex product mixtures [22][23].

Because two electron-withdrawing C_6F_5 groups of the bis-adduct **4** enhance the reactivity of the N=C–F unit, this compound easily decomposes upon column chromatography on silica gel (SiO_2) or by *Kugelrohr* distillation, which explains the low yields of **4** (*Table 1*). However, the tris-adduct **3** was found to be less reactive compared to **1**, **2**, and **4**, providing no tetrasubstituted anion (*Scheme*, *Route A*). This result is in strong contrast with the *Ruppert–Prakash* reagent, $Me_3Si(CF_3)$, which was previously reported to give perfluorinated 2,2,6,6-tetramethylpiperidine in a similar fluorinated 1-azacyclohexene system [24]. One more contrasting difference is expected for the reagent $Me_3Si(C_6F_5)$ because of the possibility to further react at the *para* position of the introduced pentafluorophenyl aromatics (*Routes B* and *C*). Thus, the reactivity of isolated **3** was further examined.

When compound **3** was reacted with 1 equiv. of $Me_3Si(C_6F_5)$, small amounts of the expected perfluorinated biphenyl compounds **5** and **6** were obtained (*Table 1*, *Entry 6*). When the reaction was conducted under more-severe conditions (50°, 48 h) with *ca.* 3 equiv. of the reagent, we were even able to isolate, apart from **5** and **6**, the perfluorinated bis-biphenyl and tris-biphenyl analogues **7a**,**b** and **8**, respectively (*Table 1*, *Entry 7*).

From a mechanistic point of view, it is noteworthy to point out two interesting features of the nucleophilic attack of a $(C_6F_5)^-$ anion on the already introduced C_6F_5 ring(s): *1*) the nucleophilic attack hardly occurred in the reactions with **2** and **4**, but in the reactions with the more-bulky compounds having at least three C_6F_5 groups, *i.e.*, compounds **3** and **5**–**7**. This means that the N=C–F unit is more reactive than the *para* position of the C_6F_5 group. *2*) The nucleophilic attack occurred only in *para* position of the C_6F_5 ring directly bonded to the heterocycles, but not on the C_6F_5 ring of the perfluorinated biphenyl group. Hence, *para* substitution stopped at the biphenyl stage, and any further extension of phenylene rings of the type $C_6F_5(C_6F_4)_n$, with $n > 1$, did not occur. It is very surprising that such a subtle structural change on the C_6F_5-ring environment leads to such a profound change in the reactivity of the *para* position of the C_6F_5 ring in the Ad_N-E mechanism. Recently, the formation of 1-H-perfluoro-4,4′-polyphenyls (1-H$(C_6F_4)_nF$) was reported by nucleophilic attack at the *para* position of a C_6F_5 ring in the reaction of $Me_3Si(C_6F_5)$ with CsF or Me_4NF [25], but no details were reported regarding compound characterization.

2. *Compound Characterization*. Compounds **2**–**8** were identified by ^{19}F- and ^{13}C-NMR, DI-MS, and MALDI-TOF-MS. Adjacent F-atom peaks were confirmed by the ^{19}F{^{19}F} homo-decoupling method. The correlations between ^{19}F and ^{13}C peaks were determined by either ^{19}F-detected ^{19}F,^{13}C-HMQC spectroscopy or partially ^{13}C{^{19}F} hetero-decoupling techniques with selective ^{19}F decoupling. As an example, the ^{19}F,^{13}C-HMQC spectrum of **3** is displayed in *Fig. 1*.

The material balance was very low in the reaction leading to the higher-substitution products (*Table 1*, *Entry 7*) due to a considerable amount of residual materials formed. Therefore, the residue was further analyzed by ^{19}F-NMR and MALDI-TOF-MS. No 3,3,5,5-tetrasubstituted pentafluorophenyl derivative **9** was detected, though. However, the MALDI-TOF experiments indicated the formation of some intriguing dimeric products, consistent with a series of signals at m/z $422+148n$ ($n=6-11$), as shown in *Fig. 2*. Since the separation of these dimers was very difficult, the underlying mechanism is not clear yet. This dimerization reaction of the six-membered ring, however, is a competitive reaction for the multiple pentafluorophenylation, and it could be

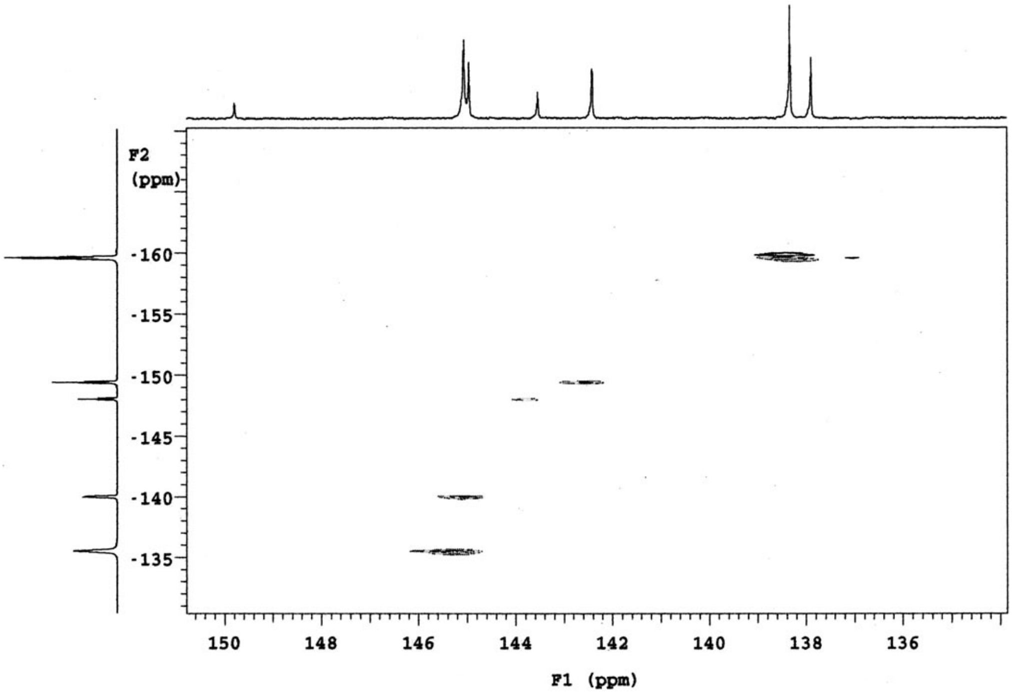


Fig. 1. *^{19}F-Detected ^{19}F,^{13}C-HMQC Spectrum of Compound* **3**. The F2 and F1 axes refer to δ_F and δ_C, resp.

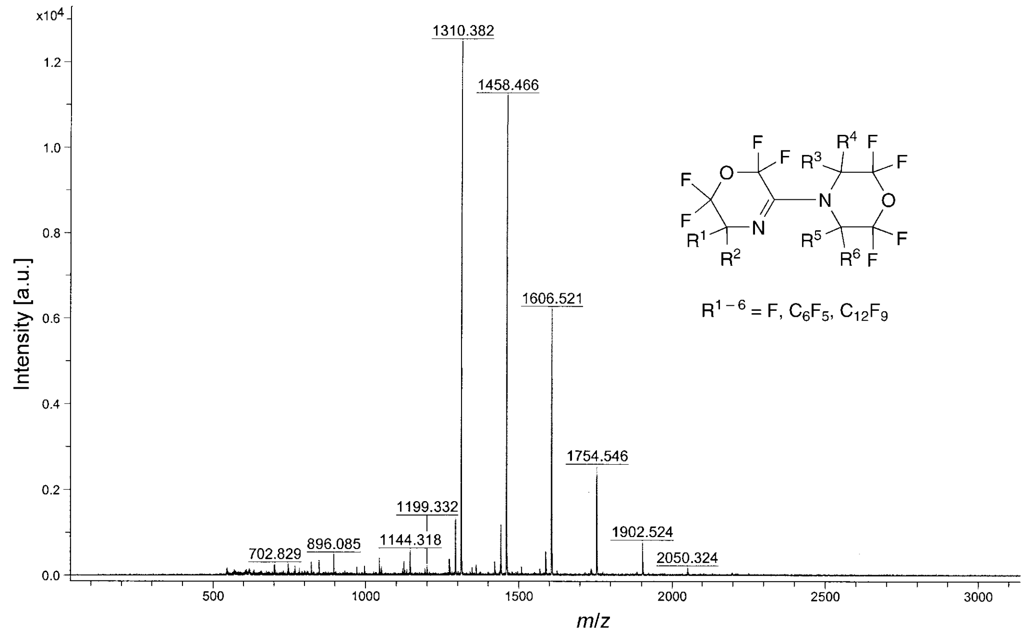


Fig. 2. *MALDI-TOF Mass spectrum of inseparable dimeric side products*

one of the reasons why no perfluorinated terphenyl derivatives were obtained under the more-severe reaction conditions.

The molecular structure of the tris-adduct **3** was unequivocally determined by X-ray crystallography (*Fig. 3*). Selected bond lengths, bond angles, and dihedral angles are listed in *Table 2*. For crystal data and structure-refinement details, see *Table 4* in the *Exper. Part*. In the asymmetric unit of the crystal, two molecules are independent. However, they can be fitted almost completely (RMS fit of 0.222 Å) by noncrystallographic rotation–inversion of 166.38°. Regarding the two geminal C_6F_5 substituents at C(12)[1], the distances C(1)–C(12) (1.533(2) Å) and C(12)–C(22) (1.543(2) Å), each between an sp^2 and an sp^3 atom, are prolonged to an equivalent length of the $C(sp^3)-C(sp^3)$ bond C(12)–C(17) (1.542(2) Å), comparable to the molecular structure of $(C_6F_5)CH_2OC(CF_3)(C_6F_5)_2$ (C–C 1.538(8) Å) [20]. Bond-angle distortions were also observed around the hetero-atoms: C(15)–O(16)–C(17) 114.79(12)°, N(13)–C(14)–C(15) 125.35(13)°, C(12)–N(13)–C(14) 118.60(12)°.

From a supramolecular point of view, compound **3** has a very interesting cap-like structure. The selection of the C_6F_5 group for a supramolecular-recognition site is based on the recent surge of reports on π–π stacking [26–28]. Further, we also expect interesting C–F···H–C interactions when using molecular systems based on several C_6F_5 groups in the vicinity of a nitrogen center, rather than in a scattered manner on the periphery of a carbon skeleton.

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[1] Arbitrary atom numbering according to *Fig. 3*.

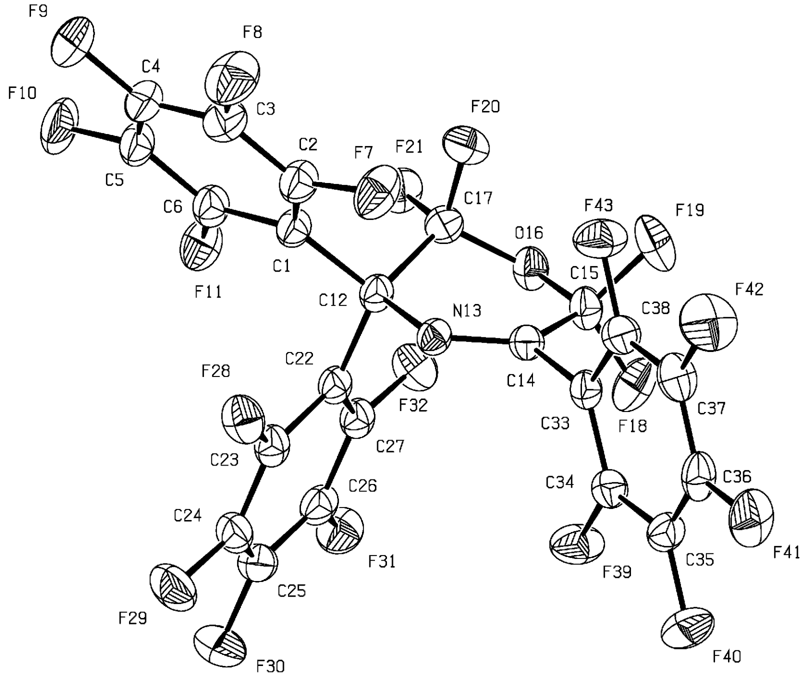

Fig. 3. *X-Ray crystal structure of* **3**. Thermal ellipsoids are shown at the 50%-probability level.

Table 2. *Selected Bond Lengths* (Å), *Bond Angles* (°), *and Torsion Angles* (°) *in the X-Ray Crystal Structure of* **3**[1])

O(16)–C(15)	1.3753(18)	O(16)–C(17)	1.3762(19)
N(13)–C(14)	1.2616(19)	N(13)–C(12)	1.4867(18)
C(14)–C(15)	1.520(2)	C(14)–C(33)	1.496(2)
C(17)–C(12)	1.542(2)	C(12)–C(22)	1.543(2)
C(1)–C(12)	1.533(2)		
C(15)–O(16)–C(17)	114.79(12)	C(14)–N(13)–C(12)	118.60(12)
N(13)–C(14)–C(15)	125.35(13)	N(13)–C(14)–C(33)	119.67(13)
N(13)–C(12)–C(22)	102.68(11)	N(13)–C(12)–C(1)	109.93(12)
O(16)–C(15)–C(14)	114.78(12)	O(16)–C(17)–C(12)	113.60(12)
N(13)–C(12)–C(17)	109.19(12)	C(17)–C(12)–C(22)	117.01(12)
C(17)–C(12)–C(1)	106.34(12)	C(22)–C(12)–C(1)	111.59(12)
N(13)–C(14)–C(15)–O(16)	−0.4(2)	N(13)–C(14)–C(33)–C(38)	−88.51(19)
N(13)–C(14)–C(33)–C(34)	92.80(18)	N(13)–C(12)–C(22)–C(23)	62.02(16)
N(13)–C(12)–C(1)–C(6)	158.18(14)		

The end-cap structure of **3** most-likely also prevented further nucleophilic attack on the C=N bond, which rationalizes why no tetra-adduct **9** was formed. This is also the reason why additional pentafluorophenylation takes place at the *para* position of existing C_6F_5 substituent(s), which, in turn, gave rise to even deeper cap structures for **5**–**8**.

3. *DFT Calculations.* Although NMR analysis is the most powerful tool for the identification of perfluorinated compounds, an assignment of each peak was difficult with our compounds, not only in ^{19}F-NMR, but also in ^{13}C-NMR, especially in the case of adducts with several C_6F_5 rings. We reported earlier that DFT calculations of various fluoro compounds, when performed at the B3LYP level using the gauge-independent atomic orbital (GIAO) level with the 6-31++G(d,q) basis set, is quite useful for the estimation of chemical shifts [29] and also for conformational analysis of highly sterically hindered polyfluoro-olefins [22]. With these powerful theoretical arsenals in our hands, we, thus, confirmed the structures of compounds **2**–**8**.

Optimized geometries of **2**–**4** were obtained by starting from modified structures based on the X-ray crystal structure of **3** by removing or adding C_6F_5 rings at the B3LYP/6-31G(d) level. On the basis of the geometries so determined, ^{19}F- and ^{13}C-NMR shieldings were calculated at the B3LYP-GIAO/6-31++G(d,p) level (*Table 3*). Note that, in the following, the atomic numbers are defined according to the *IUPAC* priority rules. For compounds **2**–**4**, the calculated (calc.) ^{19}F-NMR shieldings showed a very good relationship with experimental (exper.) values, r^2 being 0.998 (**2**), 0.997 (**3**), and 0.994 (**4**) (*Fig. 4*). The differences between the experimentally determined and the calculated values were larger for the C_4F_4NO ring ($\Delta\delta$(F) -7.58 to -11.43) than for the C_6F_5 rings ($\Delta\delta$(F) -2.95 to -5.98), except for the 3-F-atom ($\Delta\delta$(F) -1.36) of the C_4F_4NO rings (F–C=N)^2).

The calculated and experimental ^{13}C-NMR shifts of **2**–**4** also showed a very good correlation, with r^2 values of 0.991 (**2**), 0.995 (**3**), and 0.995 (**4**) (data not shown graphically). In contrast with the above ^{19}F-NMR data, the $\Delta\delta$(C) values were smaller for the C_4F_4NO ring ($\Delta\delta$(C) -2.99 to -4.44) than for the C_6F_5 rings ($\Delta\delta$(C) -7.14 to -10.15) and for the C=N group of the C_4F_4NO ring ($\Delta\delta$(C) -9.70 to -11.37). In cases of close-lying peaks, especially in the ^{13}C-NMR experiments, reversals of signal orders between calculated and experimental values were observed. Accordingly, for the compounds having close-lying peaks, NMR prediction was not perfect, and, thus, the data had to be carefully examined. In general, the calculated values were positively shifted for ^{19}F-NMR shifts, while they were negatively shifted for ^{13}C-NMR shifts due to the π-electron effect, as observed before for highly branched fluoro-olefins [22].

The more-complicated structures **5**–**8** were also successfully corroborated by means of ^{19}F- and ^{13}C-NMR analyses of experimental and DFT-calculated shielding data. The geometries of these compounds were determined at the B3LYP/6-31G(d) level, and the ^{19}F- and ^{13}C-NMR shifts were calculated from these geometries at the B3LYP-GIAO/6-31++G(d,p) level. The experimentally determined ^{19}F- and ^{13}C-NMR chemical shifts of **5**–**8** are given in the *Exper. Part*^{3}). It should be useful to pointed out some trends: *1*) the absorption signals by *o*-F-atoms (2,6-F) of the 3-C_6F_5 moiety, *i.e.*, the C_6F_5 group at the 3-position of the 1,4-oxazine ring^2) appeared at *ca.* δ(F) -140, while those of the 5-C_6F_5 group appeared at *ca.* δ(F) -135. *2*) The *p*-F-atom (4-F) of the 3-C_6F_5 group appeared at *ca.* δ(F) -148, while that of the 5-C_6F_5 group resonated at *ca.* δ(F) -149 ppm. *3*) the *m*-F-atoms (3,5-F) of the 3- and 5-C_6F_5

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^{2}) Non-systematic C-atom numbering as indicated in formula **3** (*Scheme*).

^{3}) Supplementary data regarding the *calculated* NMR chemical shifts of **5**–**8** can be obtained from the corresponding author (*M. N.*).

Table 3. *Experimentally Observed vs. Calculated* ^{19}*F- and* ^{13}*C-NMR Chemical Shifts* (in ppm) *of* **2**–**4**. For details, see text and *Exper. Part.*

Group/Atom2)	**2**		**3**		**4**	
	obs.	calc.	obs.	calc.	obs.	calc.
C_4F_nNOa)						
2-F	−72.31	−83.12	−71.78	−82.07	−75.80	−84.43
3-F					−62.81	−64.20
5-F	−99.76	−107.34				
6-F	−89.68	−99.11	−76.32	−87.75	−78.45	−88.94
3-C_6F_5						
2,6-F	−138.65	−142.11	−140.01	−142.69		
3,5-F	−158.68	−164.53	−159.42	−165.17		
4-F	−145.94	−151.85	−147.92	−153.26		
5,5-$(C_6F_5)_2$						
2,6-F			−135.55	−139.01	−135.83	−139.18
3,5-F			−159.49	−165.45	−159.46	−165.39
4-F			−149.27	−154.81	−149.26	−154.59
C_4F_nNOa)						
2-C	112.20	108.57	113.25	109.54	109.72	106.63
3-C	158.23	148.33	149.78	140.08	149.33	137.96
5-C	107.27	102.85	66.36	63.38	66.34	63.31
6-C	113.57	109.45	119.03	115.02	119.03	115.02
3-C_6F_5						
1-C	105.16	97.14	106.20	97.53		
2,6-C	144.72	134.59	145.03	135.16		
3,5-C	137.96	128.20	137.86	127.94		
4-C	144.04	134.32	143.52	134.04		
5,5-$(C_6F_5)_2$						
1-C			110.18	102.72	110.17	103.03
2,6-C			144.93	135.41	144.96	134.81
3,5-C			138.30	128.80	138.33	128.74
4-C			142.38	132.82	142.68	132.78

a) For **2**, **3**, and **4**, $n = 6$, 4, and 5, resp. (see *Scheme*).

groups appeared at *ca.* δ(F) −159. *4)* The signals of the $C_{12}F_9$ group resonated at *ca.* δ(F) −135 (2,6-F); −137 (2′,6′-F); −160 (3′,5′-F), and at −149 (4′-F), while the 3,5-F signals appeared at *ca.* δ(F) −139 and −135 in the 3- and 5-$C_{12}F_9$ moieties, respectively. The calculated ^{19}F-NMR shifts nicely correlated with the experimental values, the correlation coefficient being very high ($0.995 < r^2 < 0.998$). When looking at the overall correlation for the optimized geometries of **2**–**8**, an overall correlation coefficient r^2 of 0.995 was obtained (*Fig. 4*). Thus, the combined use of DFT-based and experimental ^{19}F-NMR experiments is very reliable in assigning pentafluorophenyl (C_6F_5) and nonafluorobiphenyl ($C_{12}F_9$) derivatives.

The following trends were observed in the experimental ^{13}C-NMR spectra of **5**–**8**: the signals for 3,5-C, 2,6-C, 4-C, 2′,6′-C, 3′,5′-C, and 4′-C appeared at δ(C) 137–145 and those for 4-C, 1-C, and 1′-C appeared at δ(C) 101–117. The corresponding calculated values, derived at the B3LYP-GIAO/6-31++G(d,p) level, also showed good correla-

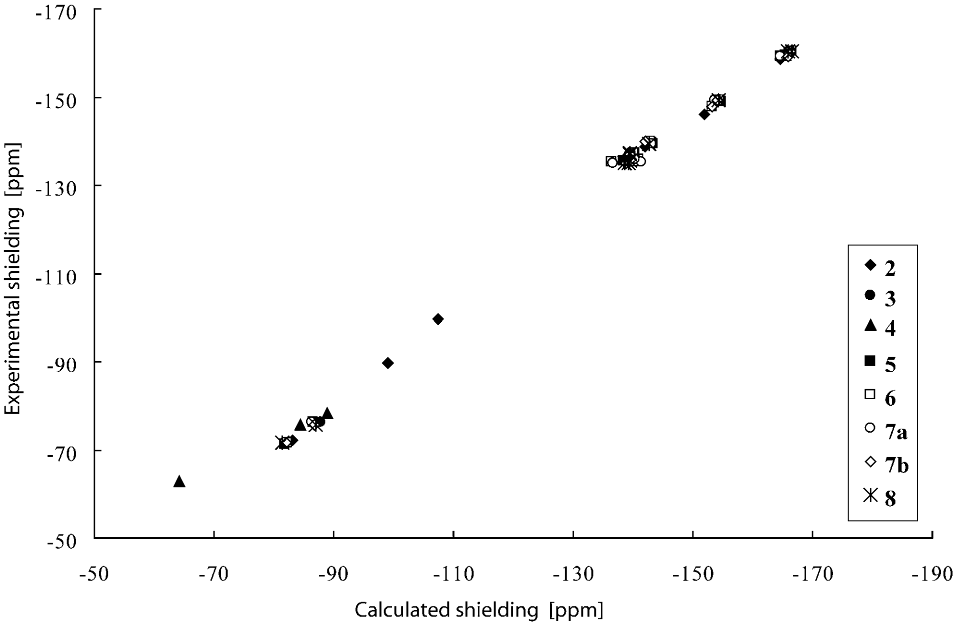

Fig. 4. *Correlation between the experimentally determined and calculated ^{19}F-NMR shieldings of* **2**–**8** *relative to $CFCl_3$ as internal reference.* A similar correlation was obtained for the corresponding ^{13}C-NMR data (not shown).

tions ($0.990 < r^2 < 0.995$). Thereby, the $\Delta\delta$ values showed some scatterings with regard to the atoms 1-C and 1′-C connecting two C_6F_5 rings. Nevertheless, the overall correlation coefficient for the ^{13}C-NMR data of **2**–**8** was still high ($r^2 = 0.992$).

Conclusions. – The pentafluorophenylation of the perfluorinated 1,4-oxazine **1** with $Me_3Si(C_6F_5)$ provided three kinds of substitution products, compounds **2**–**4**. The tris-adduct **3**, almost selectively obtained with an excess of $Me_3Si(C_6F_5)$, has a very interesting cap structure, as confirmed by X-ray crystal-structure analysis. Although the formation of the tetrasubstituted compound **9** is conceivable by reacting **3** with $Me_3Si(C_6F_5)$, further pentafluorophenylation occurred only at the *para* position of the already introduced C_6F_5 rings due to the bulky cap structure of **3**, preventing nucleophilic attack at the C=N bond of the 1,4-oxazine ring. Accordingly, five nonafluorobiphenyl-substituted compounds, **5**–**8**, were obtained by multiple substitutions of the *p*-F-atoms of the C_6F_5 groups.

The structures of **2**–**8** were determined by ^{19}F- and ^{13}C-NMR, MS, and/or X-ray crystallography. Their assignments were confirmed by comparison of DFT-calculated (B3LYP-GIAO/6-31++G(d,p)) *vs.* experimental ^{19}F- and ^{13}C-NMR chemical shifts. Since the fundamentals for the structural analysis of such perfluoroaryl systems was established in this paper, a further elongation of perfluoroaryl system will be targeted next.

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Experimental Part

General. The starting material **1** (=2,2,3,3,5,6,6-heptafluoro-3,6-dihydro-2*H*-1,4-oxazine) was prepared by pyrolysis of potassium perfluoromorpholinoacetate [30] and purified by repeated trap-to-trap distillation (final purity: 95%). Trimethyl(pentafluorophenyl)silane, $Me_3Si(C_6F_5)$, was prepared by reaction of bromopentafluorobenzene with chlorotrimethylsilane and phosphorus tris(diethylamide) [19] using *tetraglyme* as a solvent (instead of benzonitrile). Spray-dried KF was purchased from *Wako Pure Chemical Industrial, Inc.* All solvents were dried over 4-Å molecular sieves degassed by freeze-thaw cycles. All reactions were carried out under Ar atmosphere and under anh. conditions. Gases and volatile liquids were handled in a conventional *Pyrex*-glass vacuum system equipped with a *Heise–Bourdon* tube gauge and a *Televac* thermocouple gauge. Gas chromatographic (GC) analyses were performed on a *Shimadzu GC-17A* instrument with a *NEUTA BOND-1* column (60 m × 0.25 mm; 1.5 μm; *GL Science*). NMR Spectra were recorded on a *Varian Unity-Inova-300* apparatus in $CDCl_3$ in a 5-mm NMR tube at 75.42 (^{13}C) and 282.24 MHz (^{19}F); δ values rel. to $CFCl_3$ as internal reference. The ^{13}C-NMR spectra were measured using WURST modulation for complete fluorine decoupling, and using continuous wave for selective fluorine decoupling, resp. ^{19}F-detected $^{19}F,^{13}C$-HMQC spectra were recorded at 282.24 MHz with full ^{13}C decoupling using WALTZ-16 modulation and a relaxation delay of 2.4 s. GC/MS data were obtained with a *Shimadzu QP-5000* quadrupole mass spectrometer by electron-impact (EI) ionization at 70 eV on the GC column described above. Direct-inlet mass spectrometric (DI-MS) data were obtained on a *Shimadzu QP-1100EX* quadrupole mass spectrometer in EI mode at 70 eV. MALDI-TOF-MS Data were obtained on a *Bruker Daltonics AutoFLEX* time-of-flight (TOF) mass spectrometer operated under matrix-assisted laser-desorption-ionization (MALDI) conditions (matrix: '*trans*-3-indole-acrylic acid').

Reaction of **1** *with an Equimolar Amount of* $Me_3Si(C_6F_5)$. Spray-dried KF (39 mg, 0.42 mmol) in a 100-ml reaction vessel was dried at 80–90° under vacuum, and then anh. MeCN (5 ml) was added using the vacuum line. The reaction vessel was cooled to −78°, and $Me_3Si(C_6F_5)$ (0.505 g, 2.08 mmol) was added under Ar atmosphere. The mixture was then cooled to −196° and treated with **1** (0.439 g, 2.10 mmol) using the vacuum-transfer method. The mixture was then stirred at 0° for 1 h, and then at r.t. for 20 h. The volatile products were removed in vacuum at 0°. Product **2** was obtained by trap-to-trap distillation (50°/1 mmHg) in 36% isolated yield. The distilling residue was extracted with $CHCl_3$ (5 ml), and evaporation of the extract gave a mixture of **2** (41%), **3** (7%), and **4** (6.4%), as determined by ^{19}F-NMR. The sample for the identification of **2** was obtained by *Kugelrohr* distillation.

*Data of 2,2,3,3,6,6-Hexafluoro-5-(pentafluorophenyl)-3,6-dihydro-2*H*-1,4-oxazine* (**2**). ^{19}F-NMR ($CDCl_3$)[2]: −72.31 (*tm*, J=12.7, 2-F of C_4F_6NO); −89.68 (*tt*, J=5.9, 5.6, 6-F of C_4F_6NO); −99.76 (br. *t*, J=5.6, 5-F of C_4F_6NO); −138.65 (*m*, J=14.4, 12.7, 4.0, 2,6-F of C_6F_5); −145.94 (*tt*, J=21.5, 4.0, 4-F of C_6F_5); −158.68 (*m*, J=21.5, 14.4, 3,5-F of C_6F_5). ^{13}C-NMR ($CDCl_3$)[2]: 105.16 (1-C of 3-C_6F_5); 107.27 (5-C of C_4F_6NO); 112.20 (2-C of C_4F_6NO); 113.57 (6-C of C_4F_6NO); 137.96 (3,5-C of 3-C_6F_5); 144.04 (4-C of 3-C_6F_5); 144.72 (2,6-C of 3-C_6F_5); 158.23 (3-C of C_4F_6NO). GC/EI-MS: 359 (9, M^+), 193 (42), 124 (30), 100 (100), 93 (6), 69 (16).

Data of **3**. See below.

*Data of 2,2,5,6,6-Pentafluoro-3,3-bis(pentafluorophenyl)-3,6-dihydro-2*H*-1,4-oxazine* (**4**). This compound could not be isolated in pure form, neither by column chromatography (CC) on silica gel nor by *Kugelrohr* distillation, because it easily decomposed during isolation. ^{19}F-NMR ($CDCl_3$)[2]: −62.81 (*t*, J=23.4, 3-F of C_4F_5NO); −75.80 (br. *s*, 2-F of C_4F_5NO); −78.45 (br. *s*, 6-F of C_4F_5NO); −135.83 (*m*, J=15.5, 2,6-F of C_6F_5); −149.26 (*tt*, J=21.6, 5.6, 4-F of C_6F_5); −159.46 (*m*, J=21.6, 15.6, 3,5-F of C_6F_5). ^{13}C-NMR ($CDCl_3$)[2]: 66.34 (5-C of C_4F_5NO); 109.72 (2-C of C_4F_5NO); 110.17 (1-C of 5,5-$(C_6F_5)_2$); 119.03 (6-C of C_4F_5NO); 138.33 (3,5-C of 5,5-$(C_6F_5)_2$); 142.68 (4-C of 5,5-$(C_6F_5)_2$); 144.96 (2,6-C of 5,5-$(C_6F_5)_2$); 149.33 (3-C of C_4F_5NO). GC/EI-MS: 507 (41, M^+), 441 (24, $[M-COF_2]^+$), 422 (100, $[M-COF_3]^+$), 377 (17), 372 (39), 358 (11), 346 (41), 327 (77), 296 (31), 274 (38), 258 (12), 248 (27), 229 (11), 227 (11), 224 (28), 217 (77), 198 (42), 179 (42), 148 (42), 117 (26), 93 (25), 81 (15), 69 (37).

Reaction of **2** *with 2 Equiv. of* $Me_3Si(C_6F_5)$. Spray-dried KF (8 mg, 0.085 mmol) in a 100-ml reaction vessel was dried at 80–90° under vacuum, and then treated with anh. MeCN (1 ml) using the vacuum line. The vessel was cooled at −78°, and **2** (0.169 g, 0.41 mmol) was added under Ar atmosphere. The mixture was then cooled to – 196°, and treated with $Me_3Si(C_6H_5)$ (0.198 g, 0.82 mmol) *via* vacuum transfer. The mixture was stirred at 0° for 1 h, and then at r.t. for 20 h. The volatile products were removed in vacuum from the reaction mixture at 50°, and the distilling residue was extracted with $CHCl_3$ (5 ml). Evaporation of the extract gave a light-yellow solid, a mixture of **2** (4%) and **3** (78%), which was purified by CC (SiO_2; hexane) to afford pure **3** in 49% isolated yield.

*Data of 2,2,6,6-Tetrafluoro-3,3,5-tris(pentafluorophenyl)-3,6-dihydro-2*H*-1,4-oxazine* (**3**). ^{19}F-NMR ($CDCl_3$)[2]): – 71.78 (br. *s*, 2-F of C_4F_4NO); – 76.32 (br. *s*, 6-F of C_4F_4NO); – 135.55 (br. *s*, 2,6-F of 5,5-$(C_6F_5)_2$); – 140.01 (*m*, 2,6-F of 3-C_6F_5); – 147.92 (*tt*, *J* = 21.5, 4.0, 4-F of 3-C_6F_5); – 149.27 (*tt*, *J* = 21.5, 4.8, 4-F of 5,5-$(C_6F_5)_2$); – 159.42 (*dm*, *J* = 21.5, 3,5-F of 3-C_6F_5); – 159.49 (*dm*, *J* = 21.5, 3,5-F of 5,5-$(C_6F_5)_2$). ^{13}C-NMR ($CDCl_3$)[2]): 66.36 (5-C of C_4F_4NO); 106.20 (1-C of 3-C_6F_5); 110.18 (1-C of 5,5-$(C_6F_5)_2$); 113.25 (2-C of C_6F_4NO); 119.03 (6-C of C_6F_4NO); 137.86 (3,5-C of 3-C_6F_5); 138.30 (3,5-C of 5,5-$(C_6F_5)_2$); 142.38 (4-C of 5,5-$(C_6F_5)_2$); 143.52 (4-C of 3-C_6F_5); 144.93 (2,6-C of 5,5-$(C_6F_5)_2$); 149.78 (3-C of C_6F_4NO); 145.03 (2,6-C of 3-C_6F_5). DI-MS (EI): 655 (11, M^+), 589 (19, $[M - COF_2]^+$), 396 (54), 346 (60), 327 (100), 296 (31), 229 (26), 217 (25), 193 (10), 179 (40), 148 (13), 117 (10), 93 (13).

Reaction of **3** *with an Equimolar Amount of* $Me_3Si(C_6F_5)_3$. Spray-dried KF (10 mg, 0.11 mmol) in a 100-ml reaction vessel was dried at 80–90° under vacuum, and then treated with anh. MeCN (1 ml) using the vacuum line. The reaction vessel was cooled at – 78°, and **3** (0.20 g, 0.31 mmol) was added under Ar atmosphere. The mixture was cooled to – 196°, and $Me_3Si(C_6F_5)_3$ (73 mg, 0.30 mmol) was added by vacuum transfer. The mixture was stirred at 0° for 1 h, and then at r.t. for 20 h. The volatile products were removed in vacuum at 50°, and the residue was extracted with $CHCl_3$ (5 ml), which, after evaporation, gave a deep-orange viscous liquid containing **3** (72%), **5** (4.5%), and **6** (3.3%), as determined by ^{19}F-NMR. Anal. samples for the identification of **5** and **6** were obtained by CC (SiO_2; hexane/CH_2Cl_2 99 : 1).

*Data of 2,2,6,6-Tetrafluoro-5-(2,2′,3,3′,4′,5,5′,6,6′-nonafluorobiphenyl-4-yl)-3,3-bis(pentafluorophenyl)-3,6-dihydro-2*H*-1,4-oxazine* (**5**). ^{19}F-NMR ($CDCl_3$)[2]): – 71.44 (br. *s*, 2-F of C_4F_4NO); – 76.26 (br. *s*, 6-F of C_4F_4NO); – 135.48 (br. *s*, 2,6-F of C_6F_5); – 135.74 (*m*, 2,6-F of $C_{12}F_9$); – 137.25 (*m*, 2′,6′-F of C_6F_5); – 139.37 (*m*, 3,5-F of $C_{12}F_9$); – 149.10 (*tm*, *J* = 21.7, 4′-F of $C_{12}F_9$); – 149.12 (*tm*, *J* = 23.7, 4-F of C_6F_5); – 159.36 (*m*, 3,5-F of C_6F_5); – 160.21 (*m*, 3′,5′-F of $C_{12}F_9$). ^{13}C-NMR ($CDCl_3$)[2]): 66.31 (5-C of C_4F_4NO); 101.44 (1′-C of 3-$C_{12}F_9$); 110.00; (4-C of 3-$C_{12}F_9$) 110.10 (1-C of 3-$C_{12}F_9$); 110.14 (1-C of 5,5-$(C_6F_5)_2$); 113.27 (2-C of C_4F_4NO); 119.05 (6-C of C_4F_4NO); 138.03 (3′,5′-C of 3-$C_{12}F_9$); 138.28 (3,5-C of 5,5-$(C_6F_5)_2$); 142.37 (4-C of 5,5-$(C_6F_5)_2$); 142.93 (4′-C of 3-$C_{12}F_9$); 144.22 (2′,6′-C of 3-$C_{12}F_9$); 144.46 (3, 5-C of 3-$C_{12}F_9$); 144.48 (2,6-C of 3-$C_{12}F_9$); 145.03 (2,6-C of 5,5-$(C_6F_5)_2$); 149.98 (3-C of C_4F_4NO). DI-MS (EI): 803 (11, M^+), 737 (17, $[M - COF_2]^+$), 544 (20), 475 (13), 396 (12), 377 (13), 365 (12), 346 (44), 341 (14), 327 (100), 296 (27), 217 (18), 179 (15).

*Data of 2,2,6,6-Tetrafluoro-3-(2,2′,3,3′,4′,5,5′,6,6′-nonafluorobiphenyl-4-yl)-3,5-bis(pentafluorophenyl)-3,6-dihydro-2*H*-1,4-oxazine* (**6**). ^{19}F-NMR ($CDCl_3$)[2]): – 71.58 (br. *s*, 2-F of C_4F_4NO); – 76.23 (br. *s*, 6-F of C_4F_4NO); – 135.19 (br. *s*, 2,6-F of 5-C_6F_5); – 135.19 (br. *s*, 2,6-F of $C_{12}F_9$); – 135.90 (br. *s*, 3,5-F of $C_{12}F_9$); – 137.16 (*m*, 2′,6′-F of $C_{12}F_9$); – 139.97 (*m*, 2,6-F of 3-C_6F_5); – 147.84 (*t*, *J* = 21.5, 4-F of 3-C_6F_5); – 149.12 (*tm*, *J* = 21.5, 4-F of 5-C_6F_5); – 149.23 (*t*, *J* = 19.5, 4′-F of $C_{12}F_9$); – 159.27 (*m*, 3,5-F of 5-C_6F_5); – 159.34 (*m*, 3,5-F of 3-C_6F_5); – 160.34 (*m*, 3′,5′-F of $C_{12}F_9$). ^{13}C-NMR ($CDCl_3$)[2]): 66.62 (5-C of C_4F_4NO); 101.40 (1′-C of $C_{12}F_9$); 106.17 (1-C of 5-C_6F_5); 108.88 (1-C of 3-C_6F_5); 109.99 (1-C of $C_{12}F_9$); 113.26 (2-C of C_4F_4NO); 116.48 (4-C of $C_{12}F_9$); 119.01 (6-C of C_4F_4NO); 137.85 (3,5-C of 3-C_6F_5); 138.01 (3,5-C of 5-C_6F_5); 138.30 (3′,5′-C of $C_{12}F_9$); 142.47 (4-C of 5-C_6F_5); 142.93 (4-C of $C_{12}F_9$); 143.51 (4-C of 3-C_6F_5); 144.46 (2′,6′-C of $C_{12}F_9$); 144.83 (3,5-C of $C_{12}F_9$); 144.91 (2,6-C of 5-C_6F_5, 2,6-C of $C_{12}F_9$); 145.00 (2,6-C of 3-C_6F_5); 149.97 (3-C of C_4F_4NO). DI-MS (EI): 803 (21, M^+), 737 (44, $[M - COF_2]^+$), 544 (31), 494 (57), 475 (100), 444 (27), 437 (15), 406 (18), 396 (19), 377 (13), 375 (10), 365 (14), 346 (18), 327 (47), 296 (15), 247 (23), 237 (43), 229 (43), 222 (22), 217 (33), 203 (12), 193 (17), 179 (47).

Reaction of **3** *with 3 Equiv. of* $Me_3Si(C_6F_5)$ *under More-Harsh Conditions.* Spray-dried KF (10 mg, 0.11 mmol) was placed in a 100-ml reaction vessel and dried at 80–90° under vacuum. Then, anh. MeCN (1 ml) was added using the vacuum line, and the mixture was cooled at – 78°. Compound **3** (0.20 g, 0.31 mmol) was added under Ar atmosphere. The mixture was cooled at – 196°, and treated with $Me_3Si(C_6F_5)$ (0.23 g, 0.97 mmol) by vacuum transfer. The mixture was stirred at 0° for 1 h, and then heated at 50° for 48 h. The volatile products were removed in *vacuo* at 50°, and the residue was extracted with $CHCl_3$ (5 ml). Evaporation of the extract gave a deep-brown viscous liquid (0.22 g), which was subjected to CC (SiO_2; 1. hexane/CH_2Cl_2 99:1, 2. hexane/AcOEt 95:5). The less-polar fractions eluted with hexane/CH_2Cl_2 consisted of several products of similar R_f values, which were not further separated. By ^{19}F-NMR analysis, in combination with DFT calculations, compounds **3** (5.6%), **5** (8.3%), **6** (3.5%), **7a** (7.8%), **7b** (3.0%), and **8** (0.6%)[4]) could be identified (see text). The more-polar compounds trapped on top of the silica-gel column, eluted with hexane/AcOEt, formed a complex mixture of products (30 mg), as concluded by ^{19}F-NMR. According to MALDI-TOF-MS experiments, it was obvious that a homologous series of dimers had been formed (see text and *Fig. 2*).

*Data of 2,2,6,6-Tetrafluoro-3,5-bis(2,2′,3,3′,4′,5,5′,6,6′-nonafluorobiphenyl-4-yl)-3-(pentafluorophenyl)-3,6-dihydro-2*H*-1,4-oxazine* (**7a**). ^{19}F-NMR ($CDCl_3$)[2]): −71.58 (br. *s*, 2-F of C_4F_4NO); −76.20 (br. *s*, 6-F of C_4F_4NO); −135.05 (br. *s*, 2,6-F of C_6F_5); −135.22 (br. *s*, 3,5-F of 5-$C_{12}F_9$); −135.73 (*m*, 2,6-F of 3-$C_{12}F_9$); −135.77 (*m*, 2,6-F of 5-$C_{12}F_9$); −137.11 (*m*, 2′,6′-F of 5-$C_{12}F_9$); −137.26 (*m*, 2′,6′-F of 3-$C_{12}F_9$); −139.32 (*m*, 3,5-F of 3-$C_{12}F_9$); −149.01 (*tm*, $J = 21.5$, 4-F of C_6F_5); −149.14 (*tm*, $J = 19.8$, 4′-F of 5-$C_{12}F_9$); −149.21 (*tm*, $J = 21.5$, 4′-F of 3-$C_{12}F_9$); −159.15 (*m*, 3,5-F of C_6F_5); −160.23 (*m*, 3′,5′-F of 5-$C_{12}F_9$); −160.31 (*m*, 3′,5′-F of 3-$C_{12}F_9$). ^{13}C-NMR ($CDCl_3$)[2]): 66.64 (5-C of C_4F_4NO); 101.40 (1′-C of 5-$C_{12}F_9$); 101.46 (1′-C of 3-$C_{12}F_9$); 108.93 (1-C of 5-C_6F_5); 109.96 (1-C of 3-$C_{12}F_9$); 110.04 (1-C of 5-$C_{12}F_9$); 112.66 (4-C of 3-$C_{12}F_9$); 113.30 (2-C of C_4F_4NO); 116.50 (4-C of 5-$C_{12}F_9$); 119.03 (6-C of C_4F_4NO); 138.02 (3′,5′-C of 3-$C_{12}F_9$); 138.04 (3′,5′-C of 5-$C_{12}F_9$); 138.33 (3,5-C of 5-C_6F_5); 142.46 (4-C of 5-C_6F_5); 142.91 (4′-C of 5-$C_{12}F_9$); 142.95 (4′-C of 3-$C_{12}F_9$); 144.24 (2,6-C of 5-C_6F_5); 144.46 (3,5-C of 5-$C_{12}F_9$); 144.50 (2,6-C and 2′,6′-C of 3-$C_{12}F_9$; 2′,6′-C of 5-$C_{12}F_9$); 144.56 (2,6-C of 5-$C_{12}F_9$); 145.02 (3,5-C of 3-$C_{12}F_9$); 150.24 (3-C of C_4F_4NO). DI-MS (EI): 951 (13, M^+), 885 (24, $[M - COF_2]^+$), 692 (12), 544 (25), 494 (36), 475 (100), 444 (25), 437 (13), 406 (12), 377 (17), 365 (26), 346 (11), 341 (29), 327 (59), 296 (14), 272 (11), 237 (13), 217 (14), 179 (14).

*Data of 2,2,6,6-Tetrafluoro-3,3-bis(2,2′,3,3′,4′,5,5′,6,6′-nonafluorobiphenyl-4-yl)-5-(pentafluorophenyl)-3,6-dihydro-2*H*-1,4-oxazine* (**7b**). ^{19}F-NMR ($CDCl_3$)[2]): −71.72 (br. *s*, 2-F of C_4F_4NO); −75.78 (br. *s*, 6-F of C_4F_4NO); −134.84 (br. *s*, 3,5-F of 5,5-$(C_{12}F_9)_2$); −135.72 (br. *s*, 2,6-F of 5,5-$(C_{12}F_9)_2$); −137.14 (br. *s*, 2′,6′-F of 5,5-$(C_{12}F_9)_2$); −139.99 (br. *s*, 2,6-F of C_6F_5); −147.79 (*tm*, $J = 21.5$, 4-F of C_6F_5); −149.19 (*td*, $J = 21.7$, 3.95, 4′-F of 5,5-$(C_{12}F_9)_2$); −159.31 (*m*, 3,5-F of C_6F_5); −160.30 (*m*, 3′,5′-F of 5,5-$(C_{12}F_9)_2$). ^{13}C-NMR ($CDCl_3$)[2]): 66.60 (5-C of C_4F_4NO); 101.39 (1′-C of 5,5-$(C_{12}F_9)_2$); 109.93 (1-C of 3-C_6F_5); 110.02 (1-C of 5,5-$(C_{12}F_9)_2$); 113.26 (2-C of C_4F_4NO); 116.65 (4-C of 5,5-$(C_{12}F_9)_2$); 119.55 (6-C of C_4F_4NO); 137.83 (3,5-C of 3-C_6F_5); 138.00 (3′,5′-C of 5,5-$(C_{12}F_9)_2$); 142.89 (4′-C of 5,5-$(C_{12}F_9)_2$); 143.50 (4-C of 3-C_6F_5); 144.45 (3,5-C and 2′,6′-C of 5,5-$(C_{12}F_9)_2$); 144.52 (2,6-C of 5,5-$(C_{12}F_9)_2$); 144.89 (2,6-C of 3-C_6F_5); 149.78 (3-C of C_4F_4NO). DI-MS (EI): 951 (8.9, M^+), 885 (21, $[M - COF_2]^+$), 692 (34), 672 (13), 622 (100), 592 (28), 554 (19), 544 (38), 525 (27), 517 (22), 516 (23), 513 (16), 494 (42), 489 (13), 485 (15), 475 (99), 444 (24), 437 (19), 420 (15), 406 (13), 377 (35), 365 (51), 358 (13), 346 (31), 341 (34), 327 (89), 321 (26), 312 (66), 311 (42), 296 (48), 277 (21), 272 (15), 261 (13), 237 (13), 229 (24), 217 (30), 179 (23).

2,2,6,6-Tetrafluoro-3,3,5-tris(2,2′,3,3′,4′,5,5′,6,6′-nonafluorobiphenyl-4-yl)-3,6-dihydro-2H-1,4-oxazine (**8**). ^{19}F-NMR ($CDCl_3$)[2]): −71.46 (br. *s*, 2-F of C_4F_4NO); −75.71 (br. *s*, 6-F of C_4F_4NO); −134.84 (br. *s*, 3,5-F of 5,5-$(C_{12}F_9)_2$); −135.10 (*m*, 2,6-F of 3-$C_{12}F_9$); −135.68 (*m*, 2,6-F of 5,5-$(C_{12}F_9)_2$); −137.08 (*m*, 2′,6′-F of 5,5-$(C_{12}F_9)_2$); −137.28 (*m*, 2′,6′-F of 3-$C_{12}F_9$); −139.32 (br. *s*, 3,5-F of 3-$C_{12}F_9$); −149.13 (*tm*, $J = 21.5$, 4′-F of 3-$C_{12}F_9$); −149.17 (*tm*, $J = 21.5$, 4′-F of 5,5-$(C_{12}F_9)_2$); −160.29 (*m*, 3′,5′-F of 3-$C_{12}F_9$); −160.31 (*m*, 3′,5′-F of 5,5-$(C_{12}F_9)_2$). ^{13}C-NMR ($CDCl_3$)[2]): 66.91 (5-C of C_4F_4NO); 101.39 (1′-C of 3-$C_{12}F_9$); 101.75 (1′-C of 5,5-$(C_{12}F_9)_2$); 109.01 (1-C of 5,5-$(C_{12}F_9)_2$); 110.06 (1-C of 3-$C_{12}F_9$); 113.29 (2-C of C_4F_4NO); 115.08 (4-C of 3-$C_{12}F_9$); 116.24 (6-C of C_4F_4NO); 116.25 (4-C of 5,5-$(C_{12}F_9)_2$); 138.02 (3′,5′-C of 3-$C_{12}F_9$ and 3′,5′-C of 5,5-$(C_{12}F_9)_2$); 142.85 (4′-C of 3-$C_{12}F_9$); 142.90 (4′-C of 5,5-$(C_{12}F_9)_2$); 144.16 (3,5-C of 3-$C_{12}F_9$); 144.37 (3,5-C of 5,5-$(C_{12}F_9)_2$); 144.49 (2,6-C of 5,5-$(C_{12}F_9)_2$ and 2′,6′-C of 5,5-$(C_{12}F_9)_2$); 144.53 (2,6-C and 2′,6′-C of 3-$C_{12}F_9$); 150.44 (3-C of C_4F_4NO). MALDI-TOF-MS: 1099 (100, M^+), 1080 (65, $[M - F]^+$).

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[4]) Yields determined by ^{19}F-NMR integration.

Table 4. *Crystal Data and Details of Structure Refinement of* **3**

Empirical formula	$C_{22}F_{19}NO$
Formula weight	655.23
Temperature	173(2) K
Wavelength	0.71075 Å
Crystal system, space group	Monoclinic, $P\,2_1/c$
Unit-cell dimensions	$a = 12.1820(11)$ Å
	$b = 13.0800(12)$ Å
	$c = 27.184(3)$ Å
	$\beta = 91.415(2)°$
Volume	4330.2(7) $Å^3$
Z	8
Density (calc.)	2.010 Mg/m^3
Absorption coefficient	0.237 mm^{-1}
F(000)	2544
Data, restraints, parameters	9944, 0, 775
Goodness-of-fit on F^2	1.040
Final R for 8144 refl. ($I > 2\sigma(I)$)	$R1 = 0.0342$, $wR2 = 0.0840$
R Indices (all data)	$R1 = 0.0444$, $wR2 = 0.0921$
Largest diff. peak and hole	0.288, −0.247 e $Å^{-3}$

Single Crystal X-Ray Analysis of **3** (*Table 4*)[5]). Suitable crystals of **3** were obtained by recrystallization from an aerobic hexane soln. at 5° of an anal. sample obtained by CC (SiO_2; hexane). A single crystal of dimension 0.30 × 0.24 × 0.16 mm was mounted on a glass capillary and used for diffraction-data collection on a *Bruker SMART CCD* system at a temp. of 173(2) K. A total of 57,200 reflections were measured ($1.50 < \theta < 27.52°$), with 9,944 reflections being unique ($R_{int} = 0.0349$). Absorption correction by the multi-scan method (SADABS) was applied to the data set, and the maximum and minimum transmission factors were 0.963 and 0.861, resp. The structure was solved by direct methods (SHELXS-97), and the non-H-atoms were refined anisotropically by full-matrix least-squares on F^2 (SHELXL-97). The final $R1$value was 0.0342 for 8,144 reflections with $I > 2\sigma(I)$.

Computational Methods. Density-functional-theory (DFT) calculations were performed with the Gaussian98 program package [31]. All geometries were optimized at the B3LYP hybrid functional [32][33] with the 6-31G(d) basis set. Isotropic NMR-shielding tensors were calculated at the B3LYP level using the gauge-independent atomic orbital (GIAO) method [34–36] with the 6-31++G(d, p) basis set. The chemical shifts δ were calculated from the shielding (σ) as $\delta = \sigma_{ref} - \sigma$, where σ_{ref} is the ^{19}F-NMR shielding of $CFCl_3$ ($\sigma_{ref} = 179.1618$ ppm). The calculated ^{13}C-NMR shifts were derived as above, but rel. to Me_4Si ($\sigma_{ref} = 182.4602$ ppm).

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[5]) The crystallographic data of **3** have been deposited with the *Cambridge Crystallographic Data Centre* as supplementary publication number CCDC-612410. Copies of the data can be obtained at http://www.ccdc.cam.ac.uk/data_request/cif.

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