*Dedicated to Full Member of the Russian Academy of Sciences
G.A. Tolstikov on his 75th anniversary*

Organozinc Reagents from Polyfluoroarenes: Preparation and Reactions with Allyl Halides. Synthesis of Allylpolyfluoroarenes

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Abstract—Organozinc compounds of the general formula Ar_FZnX (X = Cl, Ar_F) were synthesized by reactions of Zn with chloropolyfluoroarenes and of $Zn/SnCl_2$ with polyfluoroarenes. Polyflorinated organozinc compounds reacted with allyl chloride and allyl bromide to give the corresponding allyl-substituted polyfluoroarenes. The reactions with allyl chloride were carried out in the presence of copper(I) salts (CuCl or CuI).

Introduction of an allyl group into polyfluoroarene molecules is promising from the viewpoint of synthesis of fluorine-containing analogs of antidepressants [1] and adsorbent modifiers for chromatography [2]. Methods of introduction of an allyl group are based on reactions of allyl halides with polyfluoroaromatic organometallics and of allylmagnesium halides with polyfluorinated arenes. 1-Allyl-2,3,4,5,6-pentafluoro-benzene (**I**) was prepared by reaction of allyl bromide with the Grignard compound derived from bromopentafluorobenzene (**II**) [1, 2]. Compound **I** was also synthesized in a low yield by cross coupling of iodopentafluorobenzene with allyl bromide in the presence of activated copper [3]. Pentafluorophenylcopper(I) obtained from pentafluorophenyllithium by exchange reaction reacted with allyl bromide and allyl chloride to give 60–68% of allylpentafluorobenzene (**I**) [4]. Burton et al. [5] reported on the synthesis of compound **I** from the corresponding organocadmium reagent and allyl bromide in DMF. 1-Allyl-3,5-dichloro-2,4,6-trifluorobenzene was synthesized in a high yield from tributyl(3,5-dichloro-2,4,6-trifluorophenyl)tin and allyl chloride [6]. Reactions of polyfluoroarenes with allylmagnesium bromide and chloride are characterized by a poor yield of allylpolyfluoroarenes [7, 8].

Most of the above reactions involve organolithium or organomagnesium compounds and ether solvents. With the goal of obtaining allylpolyfluoroarenes we examined reactions of allyl chloride and allyl bromide with organozinc compounds derived from polyfluoroarenes. These organometallic reagents were prepared by treatment of polyfluorinated aromatics with zinc dust in DMF. From chlorofluoroarenes **III–V** we thus obtained mixtures of the corresponding polyfluoroaryl-zinc chlorides **VIa–VIIIa** and bis(polyfluoroaryl)zincs **VIb–VIIIb**, the former prevailing [9, 10] (Scheme 1).

Scheme 1.
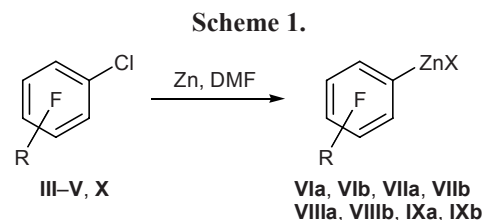
III, **VI**, R = 4-F; **IV**, **VII**, R = 4-CF$_3$; **V**, **VIII**, R = 4-Me;
X, **XI**, R = 3-CF$_3$; X = Cl (**a**), RC$_6$F$_4$ (**b**).

Compounds **III** and **IV** reacted with zinc in DMF at 135°C, and these reactions were almost complete in 4 h. By contrast, 1-chloro-2,3,5,6-tetrafluoro-4-methylbenzene (**V**) failed to react under analogous conditions. Organozinc compounds **VIIIa** and **VIIIb** were formed from arene **V** only on prolonged heating with zinc dust at elevated temperature, and the process was accompanied by formation of an appreciable amount of 2,3,5,6-tetrafluorotoluene (**IX**). Presumably, generation

of intermediate radical anions from polyfluoroarenes **III** and **IV** is more facile due to higher electron affinity of these compounds, as compared to **V**. This assumption is supported by comparison of the electron affinities of C_6F_6 and C_6F_5Cl, C_6F_6 and $C_6F_5CF_3$ [11, 12], and C_6H_5Cl and o-$CH_3C_6H_4Cl$ [13], as well as by the electrochemical reduction potentials of C_6H_5Cl and p-$CH_3C_6H_4Cl$ [14]. These data indicate that introduction of a chlorine atom or trifluoromethyl group into a polyfluoroarene molecule increases the electron affinity; therefore, introduction of a methyl group could reduce the electron affinity.
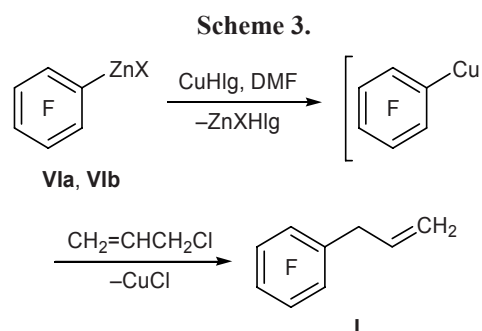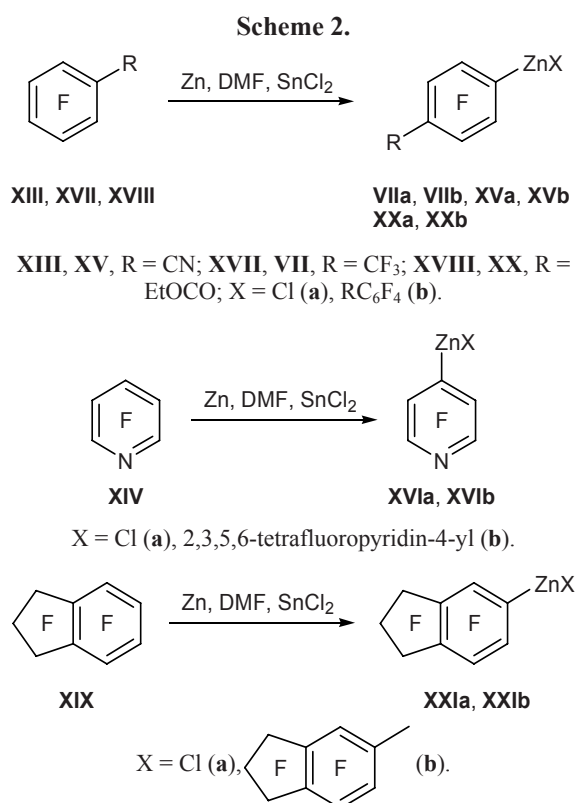
1-Chloro-2,4,5,6-tetrafluoro-3-trifluoromethylbenzene (**X**) gave rise to organozinc compounds **XIa** and **Xb** together with an appreciable amount of 1,2,3,5-tetrafluoro-4-trifluoromethylbenzene (**XII**). Presumably, apart from atmospheric moisture, dimethylformamide (solvent) can act as source of hydrogen in the formation of compound **XII**. However, this problem requires special study.

The formation of organozinc compounds from perfluoroarenes involved C–F bonds in the latter and required the presence of $SnCl_2$ as catalyst. The transformation of pentafluoroarenes **XIII** and **XIV** into the corresponding organozinc compounds **XVa**/**XVb** and **XVIa**/**XVIb** was almost complete even at room tem-

perature, whereas the reactions with **XVII–XIX** occurred at 55–65°C (Scheme 2). As above, the products were mixtures of polyfluoroarylzinc chlorides **VIIa**, **XVa**, **XVIa**, **XXa**, and **XXIa** and bis(polyfluoroaryl)zincs **VIIb**, **XVb**, **XVIb**, **XXb**, and **XXIb**, the latter prevailing.

Thus reaction of zinc with chloropolyfluoroarenes occurred at the C–Cl bond, while perfluoroarenes reacted at the C–F bond in the *para* position (C^4–F bond in pentafluoropyridine); the reactions were accompanied by replacement of the halogen atom in the same position by hydrogen (in most cases, the hydrodechlorination products were formed in small amounts).

Organozinc compounds C_6F_5ZnBr (**XXIIa**) and **VIb** obtained from bromopentafluorobenzene (**II**) and Zn in DMF reacted with allyl bromide at room temperature to give 1-allyl-2,3,4,5,6-pentafluorobenzene (**I**) whose yield reached 55% in 2 days. This reaction may be regarded as nucleophilic replacement of the bromine atom in allyl bromide by pentafluorophenyl group. After treatment of the reaction mixture with water, pentafluorobenzene (**XXIII**) was formed as a result of hydrolysis of unreacted organozinc compound. Compound **I** was also formed by reaction of allyl bromide with organozinc derivatives **VIa** and **VIb** obtained from chloropentafluorobenzene (**III**). Here, the process was accompanied by formation of allyl chloride, presumably via replacement of the bromine atom in allyl bromide by chlorine under the action of zinc chloride. When a solution of **VIa**/**VIb** and excess allyl bromide was kept for 15 days, the conversion of the organozinc compounds reached 97%, and the ratio of **I** to allyl chloride was about 4:1. Unlike allyl bromide, allyl chloride almost did not react with organozinc compounds at 20°C, whereas on heating to 60 or 100°C the yield of **I** did not exceed 5%. The process can be accelerated by addition of copper(I) salts (CuCl, CuI); in this case, the yield of **I** attains ~80%. Presumably, the catalytic effect of Cu(I) salts originates from their reaction with C_6F_5ZnX to

Scheme 2.

XIII, **XVII**, **XVIII** → **VIIa**, **VIIb**, **XVa**, **XVb** **XXa**, **XXb**

XIII, **XV**, R = CN; **XVII**, **VII**, R = CF$_3$; **XVIII**, **XX**, R = EtOCO; X = Cl (**a**), RC$_6$F$_4$ (**b**).

XIV → **XVIa**, **XVIb**

X = Cl (**a**), 2,3,5,6-tetrafluoropyridin-4-yl (**b**).

XIX → **XXIa**, **XXIb**

X = Cl (**a**), (**b**).

Scheme 3.

VIa, **VIb**

give organocopper intermediate which reacts with allyl chloride to afford compound **I** (Scheme 3).

It is known that copper(I) halides are capable of reacting with organozinc compounds to form organo-copper derivatives [15]. Taking into account that the latter are sensitive to atmospheric oxygen, the reactions of organozinc compounds in the presence of CuCl and CuI were carried out under argon. Copper(I) chloride was also used as catalyst to synthesize 1-allyl-2,3,5,6-tetrafluoro-4-trifluoromethylbenzene (**XXIV**), 1-allyl-2,3,5,6-tetrafluoro-4-methylbenzene (**XXV**), 1-allyl-2,3,4,6-tetrafluoro-5-trifluoromethylbenzene (**XXVI**), 4-allyl-2,3,5,6-tetrafluorobenzonitrile (**XXVII**), and ethyl 4-allyl-2,3,5,6-tetrafluorobenzoate (**XXVIII**) in good yields from allyl chloride and organozinc compounds **VIIa/VIIb**, **VIIIa/VIIIb**, **XIa/XIb**, **XVa/XVb**, and **XXa/XXb**. Despite different ratios of organozinc reagents **VIIa** and **VIIb** obtained from **IV** and **XVII**, they were smoothly converted into allyl-substituted polyfluoroarene **XXIV** (Scheme 4).

Scheme 4.
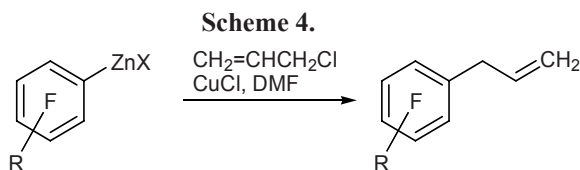
VIa, **VIb**, **VIIIa**, **VIIIb**, **XIa**, **XIb**
XVa, **XVb**, **XXa**, **XXb**   **XXIV–XXVIII**

VII, **XXIV**, R = 4-CF$_3$; **VIII**, **XXV**, R = 4-Me; **XI**, **XXVI**, R = 5-CF$_3$; **XV**, **XXVII**, R = 4-CN; **XX**, **XXVIII**, R = 6-EtOCO; X = Cl (**a**), RC$_6$F$_4$ (**b**).

Likewise, from allyl chloride and organozinc derivatives **XVIa/XVIb** and **XXIa/XXIb** we obtained 4-al-lyl-2,3,5,6-tetrafluoropyridine (**XXIX**) and 5-allyl-nonafluoroindan (**XXX**), respectively (Scheme 5).

Scheme 5.

XVIa, **XVIb**   **XXIX**

XXIa, **XXIb**   **XXX**
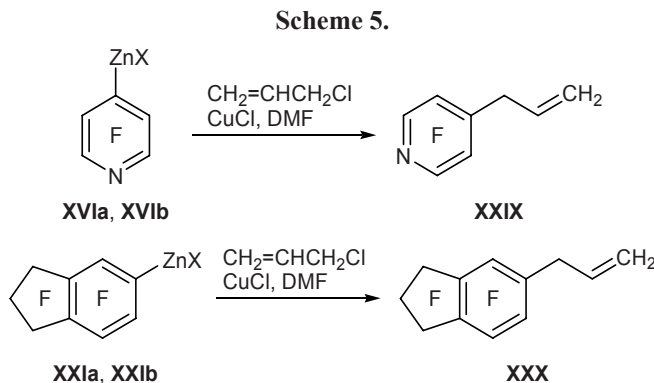
The use of ZnI$_2$ instead of copper(I) halides also ensured formation of compound **I** from C$_6$F$_5$ZnX (X =

Cl, C$_6$F$_5$) and allyl chloride, though in a poor yield. Presumably, ZnI$_2$ acts as a Lewis acid which facilitates nucleophilic replacement of the chlorine atom in allyl chloride by pentafluorophenyl group. Also, replacement of the chlorine atom in allyl chloride by iodine by the action of ZnI$_2$ cannot be ruled out. Allyl iodide is known to be more reactive than allyl chloride in nucleophilic replacement processes [16, 17].

The chemical shifts of fluorine nuclei in compounds **VIa**, **VIIa**, **XVa**, and **XVIa** in DMF were consistent with those reported for the same compounds in DMF–CDCl$_3$ [9]. Signals in the ^{19}F NMR spectra of **VIII**, **XI**, **XX**, and **XXI** were assigned taking into account general relations holding in the spectra of polyfluoroarylzinc compounds. In particular, fluorine atoms in the *ortho* position to zinc are known to resonate in a considerably weaker field, while the coupling constant $J(F^2–F^3)$ is known to increase to ~30 Hz [9, 10, 18]. The assignment of signals to Ar$_F$ZnCl (**a**) and (Ar$_F$)$_2$Zn (**b**) was facilitated by strong difference in their concentrations, which depended on the amount of chloride ions added as SnCl$_2$ or ZnCl$_2$ or liberated as a result of reaction at the C–Cl bond of the polyfluorinated substrate.

EXPERIMENTAL

The ^{1}H and ^{19}F NMR spectra were recorded on a Bruker WP-200SY spectrometer at 200 MHz for ^{1}H and 188.3 MHz for ^{19}F from reaction mixtures containing organozinc compounds in DMF or solutions in carbon tetrachloride; hexamethyldisiloxane (δ 0.04 ppm relative to TMS) and C$_6$F$_6$ (δ$_F$ –162.9 ppm relative to CCl$_3$F) were used as internal references. The IR spectra were obtained on a Hewlett–Packard Vector-22 instrument. The molecular weights and elemental compositions were determined from the high-resolution mass spectra which were run on a Finnigan MAT 8200 mass spectrometer (electron impact, 70 eV). Gas chromatographic–mass spectrometric analysis was performed on a Hewlett–Packard G1081A system consisting of an HP 5890 Series II gas chromatograph and an HP 5971 mass-selective detector (electron impact, 70 eV; 30-m×0.25-mm HP-5MS capillary column, 5% of diphenyl- and 95% of dimethylpolysiloxanes; carrier gas helium, flow rate 1 ml/min; injector temperature 280°C, ion source temperature 170°C; a.m.u. range 30–650). Gas chromatographic analysis was performed on a Hewlett–Packard HP 5980 instrument equipped with a thermal conductivity detector and a 30-m×0.52-mm HP-5 quartz capillary column; sta-

tionary phase dimethyldiphenylpolysiloxane, film thickness 2.6 μm.

Zinc dust according to GOST 12601-76 was used. Dimethylformamide was dried over solid potassium hydroxide, distilled under reduced pressure, and stored over calcium hydride. The starting compounds for the preparation of organozinc reagents had a purity of 99.1% and higher (**II**–**V**, **XIII**, **XIV**, **XVII**), 98% (**XVIII**, **XIX**), and 91% (**X**); compound **X** contained 6% of **IV** and 2% of 1-chloro-3,4,5,6-tetrafluoro-2-tri-fluoromethylbenzene. Organozinc compounds were prepared as described below; solutions were separated from zinc by decanting, and the precipitate was washed with DMF. The solutions were weighed, and the concentration of organozinc reagents was calculated with a correction for their ratio determined on the basis of the ^{19}F NMR data. The ^{19}F NMR chemical shifts of **XXIII** [19], **XII**, **IX** [10], 2,3,5,6-tetrafluoro-benzonitrile (**XXXI**) [20], 2,3,5,6-tetrafluoropyridine (**XXXII**) [21], and 1,1,2,2,3,3,4,6,7-nonafluoroindan (**XXXIII**) [22] in the NMR spectra of product mixtures were consistent with those reported in the literature. Signals from ^{19}F nuclei in the spectra of allylpoly-fluoroarenes were assigned on the basis of their fine structure and calculations of the chemical shifts according to the additivity scheme.

Pentafluorophenylzinc bromide (XXIIa) and bis-(pentafluorophenyl)zinc (VIb) were obtained from 39.22 g (600 mmol) of zinc dust and 49.39 g (200 mmol) of compound **II** in 107.8 ml (1400 mmol) of DMF at 100°C (2 h; cf. [23]); decantation gave 157.57 g of a solution containing 97% of **XXIIa** and **VIb** and 3% of **XXIII**. ^{19}F NMR spectrum, δ_F, ppm: **XXIIa**: 0.4 m (2F, 3-F, 5-F), 4.6 t (1F, 4-F, $^{3}J_{FF}$ = 19 Hz), 46.7 m (2F, 2-H, 6-F); **VIb**: 0.2 m (2F, 3-F, 5-F), 3.8 t (1F, 4-F, $^{3}J_{FF}$ = 19 Hz), 46.7 m (2F, 2-F, 6-F); **XXIIa**:**VIb** = 1.9:1.

Pentafluorophenylzinc chloride (VIa) and bis-(pentafluorophenyl)zinc (VIb) were obtained from 39.22 g (0.6 mol) of zinc dust and 40.5 g (0.2 mol) of compound **III** [9] in 107.8 ml (1.4 mol) of DMF. Decantation gave 162.39 g of a solution containing 96% of **VIa** and **VIb** and 4% of **XXIII**. ^{19}F NMR spectrum, δ_F, ppm: **VIa**: 0.5 m (2F, 3-F, 5-F), 4.7 t (1F, 4-F, $^{3}J_{FF}$ = 19 Hz), 47.2 m (2F, 2-F, 6-F); **VIb**: 0.3 m (2F, 3-F, 5-F), 3.9 t (1F, 4-F, $^{3}J_{FF}$ = 19 Hz), 46.9 m (2F, 2-F, 6-F); **VIa**:**VIb** = 4.3:1.

2,3,5,6-Tetrafluoro-4-trifluoromethylphenylzinc chloride (VIIa) and bis(2,3,5,6-tetrafluoro-4-tri-fluoromethylphenyl)zinc (VIIb). *a*. Dimethylform-amide, 32.3 ml (420 mmol), and compound **IV**, 10.85 g (43 mmol), were added to 8.43 g (129 mmol) of zinc dust, and the mixture was stirred for 4 h at 135°C. We isolated 44.84 g of a solution containing 93% of **VIIa** and **VIIb** and 7% of 1,2,4,5-tetrafluoro-3-trifluoromethylbenzene (**XXXIV**). ^{19}F NMR spectrum, δ_F, ppm: **VIIa**: 20.5 m (2F, 3-F, 5-F), 48.1 m (2F, 2-F, 6-F), 107.6 t (3F, CF$_3$, $^{4}J_{FF}$ = 20 Hz); **VIIb**: 20.5 m (2F, 3-F, 5-F), 47.7 m (2F, 2-F, 6-F), 107.7 t (3F, CF$_3$, $^{4}J_{FF}$ = 21.5 Hz); **XXXIV**: 26.2 m (2F, 3-F, 5-F), 21.4 m (2F, 2-F, 6-F), 107.2 t (3F, CF$_3$, $^{4}J_{FF}$ = 22 Hz); **VIIa**:**VIIb** = 3.4:1.

b. Dimethylformamide, 40 ml (520 mmol), and compound **XVII**, 19.95 g (84.5 mmol), were added to 30.20 g (462 mmol) of zinc dust and 0.80 g (4.2 mmol) of SnCl$_2$, and the mixture was stirred for 8 h at 55–60°C. We isolated 81.00 g of a solution containing 98% of **VIIa** and **VIIb** at a ratio of ~1:3.5 and 2% of **XXXIV**.

2,3,5,6-Tetrafluoro-4-methylphenylzinc chloride (VIIIa) and bis(2,3,5,6-tetrafluoro-4-methylphenyl)-zinc (VIIIb). Dimethylformamide, 10.8 ml (140 mmol), and compound **V**, 3.97 g (20 mmol), were added to 3.92 g (60 mmol) of zinc dust, and the mix-ture was stirred for 6 h on heating on a sand bath (bath temperature 135°C). According to the ^{19}F NMR data, the mixture contained only the initial compound. The mixture was then heated for 20 h at a bath temperature of 175–185°C. We isolated 14.17 g of a solution con-taining 61% of **VIIIa** and **VIIIb**, 27% of **IX**, and 12% of **V**. ^{19}F NMR spectrum, δ_F, ppm: **VIIIa** (major prod-uct): 18.3 m (2F, 3-F, 5-F), 44.7 m (2F, 2-F, 6-F); **VIIIb**: 18.0 m (2F, 3-F, 5-F), 44.4 m (2F, 2-F, 6-F).

2,3,4,6-Tetrafluoro-5-trifluoromethylphenylzinc chloride (XIa) and bis(2,3,4,6-tetrafluoro-5-tri-fluoromethylphenyl)zinc (XIb). Following the proce-dure described above for the synthesis of **VIIa**/**VIIb**, from 7.57 g (90 mmol) of zinc dust and 7.57 g (30 mmol) of compound **X** in 16.2 ml (210 mmol) of DMF we obtained 22.33 g of a solution containing 67% of **XIa** and **XIb** and 15% of **XII**. ^{19}F NMR spec-trum: **XIa**, δ_F, ppm: –2.6 d.d.d (1F, 3-F), 24.6 q.d.d.d (1F, 4-F), 60.2 d.d (1F, 2-F), 73.6 q.d.d (1F, 6-F), 107.5 m (3F, CF$_3$); coupling constants J_{FF}, Hz: 2-F–3-F 31.5, CF$_3$–4-F 23.5, CF$_3$–6-F 21.5, 3-F–4-F 19.0, 3-F–6-F 14.5, 2-F–4-F 9.0, 4-F–6-F 4.0; **XIb**, δ_F, ppm: –2.9 d.d.d (1F, 3-F), 23.8 q.d.d.d (1F, 4-F), 59.7 d.d (1F, 2-F), 73.1 q.d.d (1F, 6-F), ~107.5 m (3F, CF$_3$); coupling constants J_{FF}, Hz: 2-F–3-F 32.5, CF$_3$–4-F 23.5, CF$_3$–6-F 21.5, 3-F–4-F 19.0, 3-F–6-F 14.5,

2-F–4-F 9.0, 4-F–6-F 4.0; **XIa**:**XIb** = 6.7:1. Apart from compound **XII**, the solution also contained other products which were not identified.

4-Cyano-2,3,5,6-tetrafluorophenylzinc chloride (XVa) and bis(4-cyano-2,3,5,6-tetrafluorophenyl)-zinc (XVb). Dimethylformamide, 16.2 ml (210 mmol), and nitrile **XIII**, 5.79 g (30 mmol), were added to 5.88 g (90 mmol) of zinc dust and 57 mg (3.0 mmol) of SnCl$_2$, and the mixture was stirred for 6 h at room temperature. We isolated 21.80 g of a solution containing 98% of **XVa** and **XVb** and 2% of **XXXI**. ^{19}F NMR spectrum, δ_F, ppm: **XVa**: 27.6 m (2F, 3-F, 5-F), 48.9 m (2F, 2-F, 6-F); **XVb**: 27.4 m (2F, 3-F, 5-F), 48.5 m (2F, 2-F, 6-F); **XVa**:**XVb** = 1:1.8.

2,3,5,6-Tetrafluoropyridin-4-ylzinc chloride (XVIa) and bis(2,3,5,6-tetrafluoropyridin-4-yl)zinc (XVIb). Dimethylformamide, 8.1 ml (105 mmol), and compound **XIV**, 2.54 g (15 mmol), were added to 2.94 g (45 mmol) of zinc dust and 28 mg (1.5 mmol) of SnCl$_2$, and the mixture was stirred for 12 h at room temperature. We isolated 10.13 g of a solution containing 94% of **XVIa** and **XVIb** and 2% of **XXXII**. ^{19}F NMR spectrum, δ_F, ppm: **XVIa**: 41.8 m (2F, 3-F, 5-F), 65.5 m (2F, 2-F, 6-F); **XVIb**: 41.4 m (2F, 3-F, 5-F), 65.1 m (2F, 2-F, 6-F); **XVIa**:**XVIb** = 1:1.8.

4-Ethoxycarbonyl-2,3,5,6-tetrafluorophenylzinc chloride (XXa) and bis(4-ethoxycarbonyl-2,3,5,6-tetrafluorophenyl)zinc (XXb). Dimethylformamide, 27 ml (350.9 mmol), and benzoate **XVIII**, 13.00 g (54.1 mmol), were added to 17.68 g (270.5 mmol) of zinc dust and 0.51 g (2.7 mmol) of SnCl$_2$, and the mixture was stirred for 8 h at 60–65°C. We obtained 44.21 g of a solution containing 98% of **XXa** and **XXb**. ^{19}F NMR spectrum, δ_F, ppm: **XXa**: 21.7 m (2F, 3-F, 5-F), 46.9 m (2F, 2-F, 6-F); **XXb**: 21.5 m (2F, 3-F, 5-F), 46.4 m (2F, 2-F, 6-F); **XXa**:**XXb** = 1:4.9.

1,1,2,2,3,3,4,6,7-Nonafluoroindan-5-ylzinc chloride (XXIa) and bis(1,1,2,2,3,3,4,6,7-nona-fluoroindan-5-yl)zinc (XXIb). Dimethylformamide, 16.2 ml (210 mmol), and polyfluoroindan **XIX**, 8.94 g (30 mmol), were added to 5.88 g (90 mmol) of zinc dust and 0.57 g (3 mmol) of SnCl$_2$, and the mixture was stirred for 16 h at 60–65°C. We obtained 32.85 g of a solution containing 98% of **XXIa** and **XXIb** and 2% of **XXXIII**. ^{19}F NMR spectrum, δ_F, ppm: **XXIa**: 16.6 d.d.m (1F, 7-F), 34.6 m (2F, 2-F), 57.2 m and 57.6 m (2F, 1-F, 3-F), 63.4 d (1F, 6-F), 71.2 d (1F, 4-F); J(6-F,7-F) = 29.5, J(4-F,7-F) = 24 Hz; **XXIb**: 16.2 d.d.m (1F, 7-F), 34.6 m (2F, 2-F), 57.3 m and 57.7 m (2F, 1-F, 3-F), 62.9 d (1F, 6-F), 70.7 d (1F,

4-F); J(6-F,7-F) = 31, J(4-F,7-F) = 23 Hz; **XXIa**: **XXIb** = 1:1.2.

1-Allyl-2,3,4,5,6-pentafluorobenzene (I). *a*. Allyl bromide, 1.74 g (14.4 mmol), was added to 11.30 g (14.0 mmol; hereinafter, the amount of the organozinc reagent per aromatic ring is given) of a solution containing organozinc compounds **XXIIa** and **VIb**, and the mixture was kept for 2 days at room temperature. The mixture was treated with 10 ml of water and was subjected to steam distillation. The organic layer was separated and dried over MgSO$_4$. We thus isolated 2.13 g of a mixture containing (according to the GLC data), 60% of **I** (yield 44%), 28% of **XXIII**, and 10% of allyl bromide.

b. Allyl bromide, 1.74 g (14.4 mmol), was added to 11.60 g of a solution containing 13.7 mmol of organozinc compounds **VIa** and **VIb**, and the mixture was kept for 2 days at room temperature. According to the ^{19}F NMR data, it contained 63% of **VIa** and **VIb**, 32% of **I**, and 5% of **XXIII**. The mixture was treated as described above in *a* to isolate 2.59 g of a mixture containing (GLC) 29% of **I** (yield 27%), 43% of **XXIII**, 20% of allyl bromide, and 5% of allyl chloride.

c. Allyl bromide, 25.41 g (210 mmol), was added to 66.88 g of a solution containing 79 mmol of organozinc compounds **VIa** and **VIb**, and the mixture was kept for 15 days at room temperature. According to the ^{19}F NMR data, the mixture contained 3% of **VIa** and **VIb**, 89% of **I**, and 8% of **XXIII**. The mixture was diluted with 300 ml of water and extracted with carbon tetrachloride (3×40 ml), and the extract was dried over MgSO$_4$. According to the ^{19}F and ^{1}H NMR data, the extract contained allyl chloride and compound **I** at a ratio of 1:4. A fraction with bp 32–42°C, 0.51 g, was distilled off; it contained (GLC) 68% of allyl chloride which was also identified by GC–MS ([*M*]$^+$ 76).

d. Allyl chloride, 1.10 g (14.4 mmol), was added to 11.60 g of a solution containing 13.7 mmol of organozinc compounds **VIa** and **VIb**, and the mixture was kept for 2 days at room temperature. According to the ^{19}F NMR data, it contained 93% of initial compounds **VIa** and **VIb** and 7% of **XXIII**. The mixture was treated as described above in *a* to isolate 1.59 g of a mixture containing (GLC) 0.3% of **I** (yield 0.2%), 74% of **XXIII**, and 22% of allyl chloride.

e. Likewise, the reaction at 60°C (20 h) gave 1.40 g of a mixture containing (GLC) 4.1% of **I** (yield 2%); in the reaction carried out at 100°C (4 h), the yield of **I** was 5% (fraction 5.1% in the product mixture, according to the GLC data).

f. A mixture of 11.60 g of a solution containing 13.7 mmol of organozinc compounds **VIa** and **VIb**, 1.10 g (14.4 mmol) of allyl chloride, and 47 mg (1.4 mmol) of ZnI$_2$ was heated for 20 h at 60°C. The mixture was cooled to room temperature and treated as described above in *a*. We isolated 2.0 g of a product mixture containing (GLC) 42.4% of **I** (yield 30%), 44% of **XXIII**, and 6% of allyl chloride.

g. A mixture of 11.60 g of a solution containing 13.7 mmol of organozinc compounds **VIa** and **VIb**, 1.10 g (14.4 mmol) of allyl chloride, and 0.27 g (1.4 mmol) of CuI was heated for 4 h at 60°C under argon. The mixture was cooled and treated as described above in *a*. We isolated 2.47 g of a product mixture containing (GLC) 95% of **I** (yield 82%) and 3% of **XXIII**.

h. Following the procedure described above in *g* but using 27 mg (0.14 mmol) of CuI we obtained 2.43 g of a product mixture containing (GLC) 93% of **I** (yield 79%) and 3% of **XXIII**.

i. A mixture of 11.60 g of a solution containing 13.7 mmol of organozinc compounds **VIa** and **VIb**, 1.10 g (14.4 mmol) of allyl chloride, and 14 mg (0.14 mmol) of CuCl was heated for 4 h under argon at a bath temperature of 60–65°C (oil bath). The mixture was cooled and treated as described above in *a*. We isolated 2.45 g of a product mixture containing (GLC) 92% of **I** (yield 79%) and 4% of **XXIII**. Compound **I** was purified by vacuum distillation, bp 72–76°C (30 mm); published data [2]: bp 148–150°C. ^{1}H NMR spectrum, δ, ppm: 3.42 d.m (2H, CH$_2$, $^3J_{HH}$ = 6.3 Hz), 5.02–5.11 m (2H, =CH$_2$), 5.83 m (1H, CH=). ^{19}F NMR spectrum, δ$_F$, ppm: –0.7 m (2F, 3-F, 5-F), 4.7 t (1F, 4-F, $^3J_{FF}$ = 20.5 Hz), 17.7 m (2F, 2-F, 6-F) (cf. [2]).

The other allyl-substituted polufluoroarenes were synthesized according to similar procedures.

1-Allyl-2,3,5,6-tetrafluoro-4-trifluoromethylbenzene (XXIV). *a*. The reaction was carried out using 15.73 g of a solution containing 14.0 mmol of organozinc compounds **VIIa** and **VIIb** (prepared according to method *a*), 1.15 g (15 mmol) of allyl chloride, and 15 mg (0.15 mmol) of CuCl. We isolated 3.52 g of a product mixture containing (GLC) 88.3% of **XXIV** (yield 86%).

b. The reaction was carried out using 14.42 g of a solution containing 14.7 mmol of organozinc compounds **VIIa** and **VIIb** (prepared according to method *b*), 1.15 g (15 mmol) of allyl chloride, and 15 mg (0.15 mmol) of CuCl to isolate 3.33 g of a product

containing (GLC) 95% of **XXIV** (yield 83%). The product was purified by vacuum distillation, bp 43–44°C (3 mm). IR spectrum, ν, cm^{-1}: 3098, 3019, 2990, 2939, 1662, 1642, 1496, 1323, 1218, 1187, 1155, 984. UV spectrum, λ$_{max}$, nm (logε): 203 (4.05), 274 (3.33). ^{1}H NMR spectrum, δ, ppm: 3.51 d.m (2H, CH$_2$, $^3J_{HH}$ = 6.3 Hz), 5.08–5.16 m (2H, =CH$_2$), 5.84 m (1H, CH=). ^{19}F NMR spectrum, δ$_F$, ppm: 19.5 m (2F, 2-F, 6-F), 20.9 m (2F, 3-F, 5-F), 105.3 t (3F, CF$_3$, $^3J_{FF}$ = 21.5 Hz). Mass spectrum, *m/z* (I_{rel}, %): 259 (10), 258 (100) $[M]^+$, 239(30) $[M – F]^+$, 231(31) $[M – C_2H_3]^+$, 189 (43) $[M – CF_3]^+$. Found, %: C 46.51; H 1.84; F 51.66. $[M]^+$ 258.02794. C$_{10}$H$_5$F$_7$. Calculated, %: C 46.53; H 1.95; F 51.52. *M* 258.02794.

1-Allyl-2,3,5,6-tetrafluoro-4-methylbenzene (XXV). The reaction was carried out using 10.72 g of a solution containing 9.2 mmol of organozinc compounds **VIIIa** and **VIIIb**, 1.10 g (14.4 mmol) of allyl chloride, and 14 mg (0.14 mmol) of CuCl. We isolated 1.89 g of a product mixture containing (GLC) 63.4% of **XXV** (yield 64%), 18% of **IX**, and 10% of **V**. Compound **XXV** was purified by vacuum distillation, bp 49–51°C (3 mm). UV spectrum, λ$_{max}$, nm (logε): 207 (4.00), 263 (2.94). ^{1}H NMR spectrum, δ, ppm: 2.25 t (3H, CH$_3$, $^4J_{HF}$ = 2.1 Hz), 3.41 d.m (2H, CH$_2$, $^3J_{HH}$ = 6.3 Hz), 5.05 m (2H, =CH$_2$), 5.84 m (1H, CH=). ^{19}F NMR spectrum, δ$_F$, ppm: 15.8 m (2F, 2-F, 6-F), 17.3 m (2F, 3-F, 5-F). Mass spectrum, *m/z* (I_{rel}, %): 205 (10), 204 (100) $[M]^+$, 203 (15), 189 (41) $[M – CH_2]^+$, 185 (14) $[M – F]^+$, 177 (59) $[M – C_2H_3]^+$. Found: $[M]^+$ 204.05525. C$_{10}$H$_8$F$_4$. Calculated: *M* 204.05621.

1-Allyl-2,3,4,6-tetrafluoro-5-trifluoromethyl-benzene (XXVI). The reaction was carried out with 11.90 g of a solution containing 10.6 mmol of organo-zinc compounds **XIa** and **XIb**, 1.10 g (14.4 mmol) of allyl chloride, and 14 mg (0.14 mmol) of CuCl. We isolated 2.18 g of a product mixture containing (GLC) 71.7% of **XXVI** (yield 66%) and 8% of **XII**. Compound **XXVI** was purified by vacuum distillation, bp 59–61°C (8 mm). IR spectrum, ν, cm^{-1}: 3091, 2990, 2931, 1651, 1627, 1343, 1220, 1182, 1153, 979. UV spectrum, λ$_{max}$, nm (logε): 202 (3.75), 267 (2.82). ^{1}H NMR spectrum, δ, ppm: 3.43 d.m (2H, CH$_2$, $^3J_{HH}$ = 6.4 Hz), 5.04–5.13 m (2H, =CH$_2$), 5.83 m (1H, CH=). ^{19}F NMR spectrum, δ$_F$, ppm: –0.7 t.d (1F, 3-F), 26.3 q.d.d.d (1F, 4-F), 31.9 d.d.d (1F, 2-F), 42.2 m (1F, 6-F), 105.4 t (3F, CF$_3$); *J*(CF$_3$,4-F) = 23.0, *J*(CF$_3$,6-F) = 22.5, *J*(2-F,3-F) = 21.5, *J*(3-F,4-F) = 20.5, *J*(3-F,6-F) = 11.5, *J*(2-F,4-F) = 9.5, *J*(2-F,6-F) = 6.0, *J*(4-F,6-F) = 4.0 Hz. Mass spectrum, *m/z* (I_{rel}, %):

259 (10), 258.00 (100) $[M]^+$, 257 (12), 239 (31) $[M -$ F]$^+$, 237 (8), 231 (69) $[M - C_2H_3]^+$. Found, %: C 47.27; H 2.09; F 52.05. $[M]^+$ 238.03015. $C_{10}H_5F_7$. Calculated, %: C 46.53; H 1.95; F 51.52. M 258.02794.

4-Allyl-2,3,5,6-tetrafluorobenzonitrile (XXVII). The reaction was carried out using 21.80 g of a solution containing 29.2 mmol of organozinc compounds **XVa** and **XVb**, 2.29 g (30 mmol) of allyl chloride, and 30 mg (0.3 mmol) of CuCl. We isolated 5 g of a product containing (GLC) 92.8% of **XXVII** (yield 74%), which was purified by vacuum distilation, bp 60–61°C (3 mm). IR spectrum, ν, cm^{-1}: 3088, 3019, 2987, 2931, 2247, 1656, 1641, 1494, 1313, 1299, 983. UV spectrum, λ_{max}, nm (log ε): 202 (4.21), 230 (4.32), 236 (4.30), 288 (3.49). ^{1}H NMR spectrum, δ, ppm: 3.54 d.m (2H, CH$_2$, $^3J_{HH}$ = 6.4 Hz), 5.08–5.18 m (2H, =CH$_2$), 5.85 m (1H, CH=). ^{19}F NMR spectrum, δ_F, ppm: 20.9 m (2F, 3-F, 5-F), 28.4 m (2F, 2-F, 6-F). Mass spectrum, m/z (I_{rel}, %): 216 (10), 215 (100) $[M]^+$, 214 (14), 196 (24) $[M - F]^+$, 194 (29), 188 (53) $[M - C_2H_3]^+$. Found: $[M]^+$ 262.06097. $C_{10}H_5F_4N$. Calculated: M 262.06168.

Ethyl 4-allyl-2,3,5,6-tetrafluorobenzoate (XXVIII) was synthesized using 12.50 g of a solution containing 14.7 mmol of organozinc reagents **XXa** and **XXb,** 1.15 g (15 mmol) of allyl chloride, and 15 mg (0.15 mmol) of CuCl. We isolated 3.54 g of a product containing (GLC) 94% of **XXVIII** (yield 87%), which was purified by vacuum distillation, bp 119–120°C (6 mm). IR spectrum, ν, cm^{-1}: 3088, 2986, 2939, 2910, 2881, 1742, 1656, 1641, 1486, 1316, 1217, 983. UV spectrum, λ_{max}, nm (log ε): 205 (4.06), 224 (4.01), 275 (3.23). ^{1}H NMR spectrum, δ, ppm: 1.39 t (3H, CH$_3$, $^3J_{HH}$ = 7.1 Hz), 3.47 d.m (2H, CH$_2$, $^3J_{HH}$ = 6.4 Hz), 4.38 q (2H, OCH$_2$, $^3J_{HH}$ = 7.1 Hz), 5.10 m (2H, =CH$_2$), 5.84 m (1H, CH=). ^{19}F NMR spectrum, δ_F, ppm: 18.1 m (2F, 3-F, 5-F), 21.4 m (2F, 2-F, 6-F). Mass spectrum, m/z (I_{rel}, %): 263 (6), 262 (45) $[M]^+$, 237 (27) $[M - C_2H_4]^+$, 218 (17), 217 (100) $[M - C_2H_5O]^+$. Found, %: C 55.76; H 3.91; F 29.35. $[M]^+$ 262.06097. $C_{12}H_{10}F_4O_2$. Calculated, %: C 54.97; H 3.84; F 28.98. M 262.06168.

4-Allyl-2,3,5,6-tetrafluoropyridine (XXIX) was synthesized using 9.70 g of a solution containing 13.5 mmol of organozinc compounds **XVIa** and **XVIb**, 1.10 g (14.4 mmol) of allyl chloride, and 14 mg (0.14 mmol) of CuCl. The crude product, 2.08 g, contained (GLC) 92.7% of **XXIX** (yield 75%). The product was purified by vacuum distillation, bp 79–80°C (10 mm). IR spectrum, ν, cm^{-1}: 3091, 2997, 2931,

1647, 1595, 1471, 1253, 971. UV spectrum, λ_{max}, nm (log ε): 202 (3.73), 265 (3.56), 541 (1.98). ^{1}H NMR spectrum, δ, ppm: 3.54 d.m (2H, CH$_2$, $^3J_{HH}$ = 6.3 Hz), 5.12–5.20 m (2H, =CH$_2$), 5.85 m (1H, CH=). ^{19}F NMR spectrum, δ_F, ppm: 15.9 m (2F, 3-F, 5-F), 70.9 m (2F, 2-F, 6-F). Mass spectrum, m/z (I_{rel}, %): 192 (9), 191 (100) $[M]^+$, 190 (20) $[M - H]^+$, 172 (50) $[M - F]^+$, 171 (17), 170 (30), 164 (22) $[M - C_2H_3]^+$. Found, %: C 51.22; H 2.32; F 39.89; N 7.11. $[M]^+$ 191.03559. $C_8H_5F_4N$. Calculated, %: C 50.27; H 2.64; F 39.76; N 7.33. M 191.03581.

5-Allyl-1,1,2,2,3,3,4,6,7-nonafluoroindan (XXX) was synthesized using 15.56 g of a solution containing 13.8 mmol of organozinc compounds **XXIa** and **XXIb**, 1.72 g (22.5 mmol) of allyl chloride, and 22 mg (0.22 mmol) of CuCl. We isolated 3.60 g of a product mixture containing (GLC) 87% of **XXX** (yield 71%) and 4% of **XXXIII**. Compound **XXX** was purified by vacuum distillation, bp 82–83°C (2 mm). IR spectrum, ν, cm^{-1}: 3091, 2990, 1643, 1501, 1392, 1330, 1256, 1158, 953. UV spectrum, λ_{max}, nm (log ε): 203 (4.12), 273 (3.21). ^{1}H NMR spectrum, δ, ppm: 3.55 d.m (2H, CH$_2$, $^3J_{HH}$ = 6.4 Hz), 5.15–5.20 m (2H, =CH$_2$), 5.85 m (1H, CH=). ^{19}F NMR spectrum, δ_F, ppm: 20.1 t.t (1F, 7-F), 31.6 quint (2F, 2-F), 35.8 d.d (1F, 6-F), 42.3 d.q (1F, 4-F), 54.3 m and 54.7 m (2F, 1-F, 3-F); J(6-F,7-F) = 21.0, J(4-F,7-F) = 20.5, J(4-F,6-F) = 8.5, J(3-F,4-F) = 8.0, J(1-F,7-F) = 7.0, J(2-F,1-F) = J(2-F,3-F) = 4.5 Hz. Mass spectrum, m/z (I_{rel}, %): 321 (17), 320 (100) $[M]^+$, 319 (11), 301 (25) $[M - F]^+$, 293 (43) $[M - C_2H_3]^+$. Found, %: C 45.11; H 1.67; F 53.48. $[M]^+$ 320.02436. $C_{12}H_5F_9$. Calculated, %: C 45.02; H 1.57; F 53.41. M 320.02474.

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