

Reactions of polyfluoroarylzinc compounds with Vilsmeier-Haack reagent; new synthesis of polyfluorinated aromatic aldehydes and acetals

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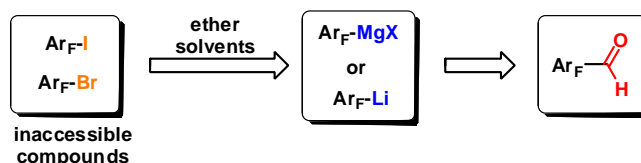
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Abstract: Polyfluoroarylzinc compounds were prepared from chloropentafluorobenzene, 1,4-dibromo-2,3,5,6-tetrafluorobenzene and perfluoroarenes. Polyfluoroaromatic aldehydes were synthesized by reactions of polyfluoroarylzinc compounds with Vilsmeier-Haack reagent formed from oxalyl chloride and DMF, and subsequent treatment of the reaction mixtures with water. When methanol was used instead of water polyfluorinated acetals were obtained.

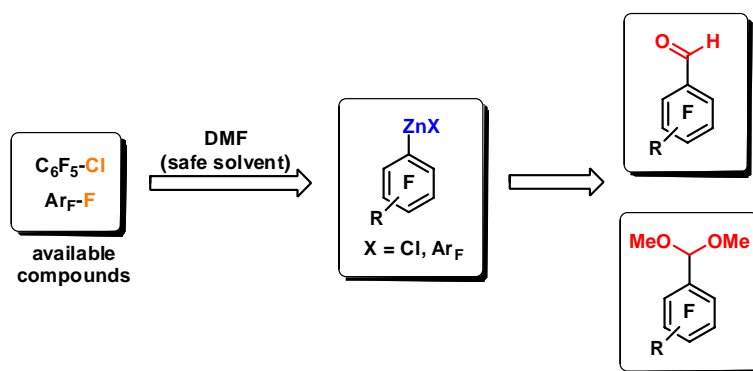
Keywords: polyfluoroarylzinc compounds; Vilsmeier-Haack reagent; aldehydes; acetals.

INTRODUCTION

Polyfluoroaromatic aldehydes are used as starting materials to produce fluorine-containing products that are of interest for agriculture, medicine and electronics. Polyfluorinated aromatic aldehydes are synthesized mainly from iodo- and bromopolyfluoroarenes. For this at the beginning these arenes are converted into polyfluoroaryllithium and polyfluoroarylmagnesium compounds in ether or THF from which then polyfluoroaromatic aldehydes were synthesized [1]. Nevertheless these aldehydes are not easily accessible.



In this connection it was worthwhile to develop another method for the synthesis of polyfluoroaromatic aldehydes on the basis polyfluoroarylzinc compounds. The latter are readily available from chloropentafluorobenzene, perfluoroarenes and Zn using DMF as safe solvent. Polyfluoroarylzinc compounds can also be used for synthesis of polyfluoroaromatic acetals.

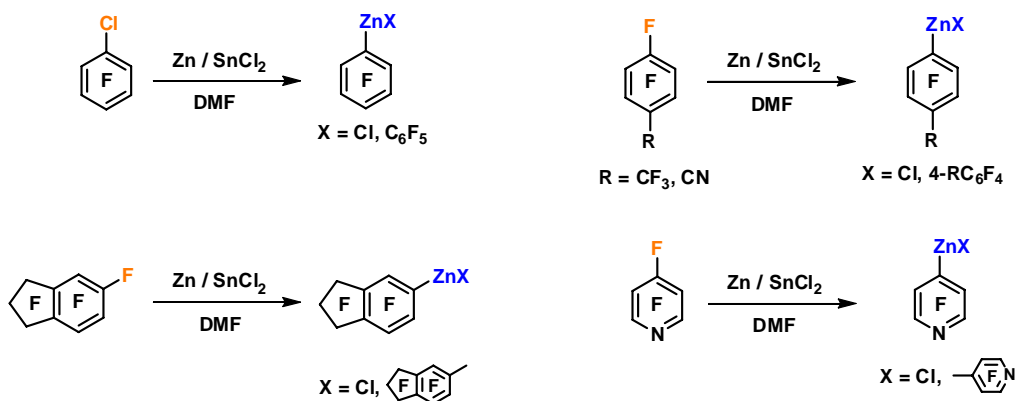


RESULTS AND DISCUSSION

Preparation of polyfluoroarylzinc compounds.

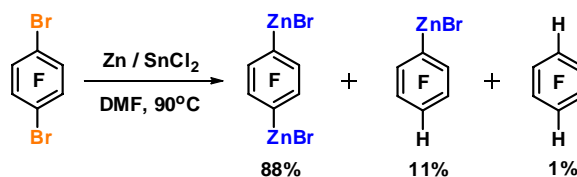
Polyfluoroarylzinc compounds were prepared from chloropentafluorobenzene, heptafluorotoluene, pentafluorobenzonitrile, perfluoroindan and pentafluoropyridine by their reactions with Zn in the presence of SnCl_2 in DMF [2, 3] (Scheme 1).

Scheme 1.



We have shown that 1,4-dibromo-2,3,5,6-tetrafluorobenzene is reacted with zinc dust in the presence of SnCl_2 in DMF at 90°C to give a mixture consisted of *p*-tetrafluorophenylenedizinc bromide, 2,3,5,6-tetrafluorophenylzinc bromide and 1,2,4,5-tetrafluorobenzene (Scheme 2).

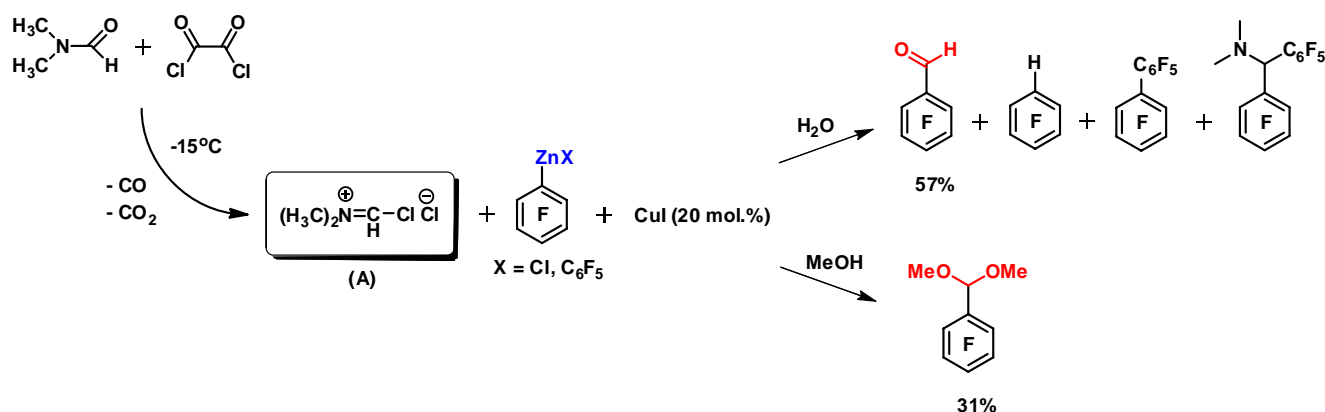
Scheme 2.



Synthesis of polyfluorinated aromatic aldehydes and acetals.

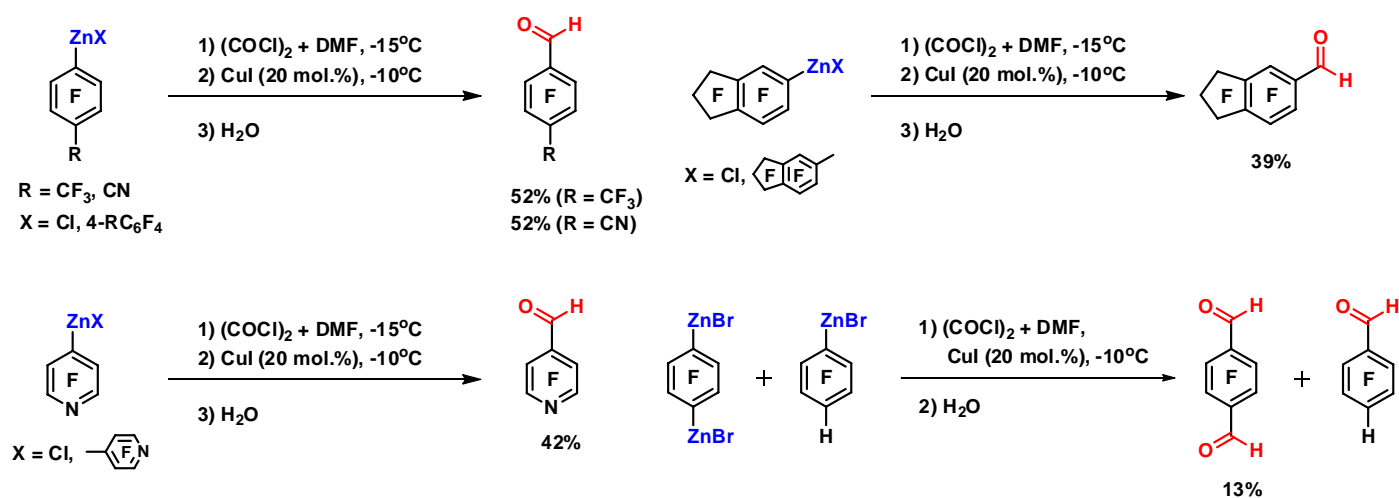
The reaction of pentafluorophenylzinc compounds with Vilsmeier-Haack reagent (A) formed from oxalyl chloride and DMF was performed in the presence of CuI as a catalyst in DMF. Subsequent hydrolysis of the reaction mixture gave pentafluorobenzaldehyde as a main product along with pentafluorobenzene, decafluorobiphenyl and N,N-dimethyl-bis(pentafluorophenyl)methanamine as by-products (Scheme 3). When methanol was used instead of water, 1-(dimethoxymethyl)-2,3,4,5,6-pentafluorobenzene was obtained.

Scheme 3.



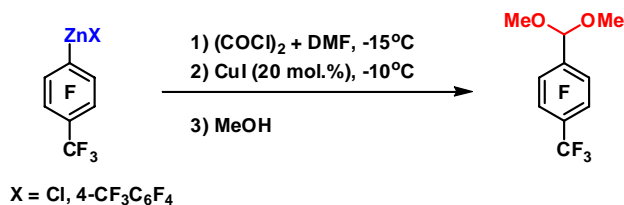
Similar reactions of other polyfluoroarylzinc compounds with Vilsmeier-Haack reagent (A) resulted in the corresponding polyfluoroaromatic aldehydes. The reaction of mixture of organozinc compounds obtained from 1,4-dibromo-2,3,5,6-tetrafluorobenzene with reagent (A) gave 2,3,5,6-tetrafluoroterephthalic aldehyde and 2,3,5,6-tetrafluorobenzaldehyde (Scheme 4).

Scheme 4.



1-(Dimethoxymethyl)-4-(trifluoromethyl)-2,3,5,6-tetrafluorobenzene was prepared from 4-(trifluoromethyl)-2,3,5,6-tetrafluorophenylzinc compounds and reagent (A) by treating reaction mixture with methanol (Scheme 5).

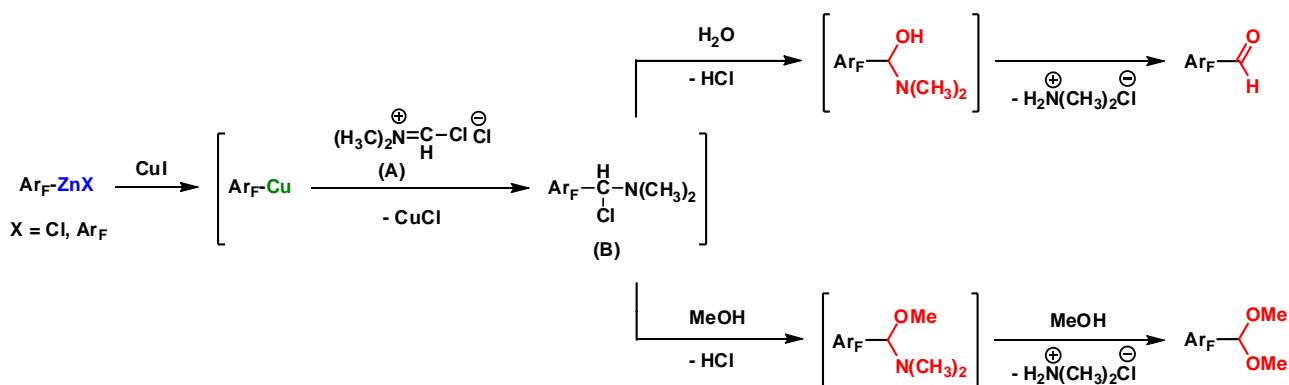
Scheme 5.



Schemes of the formation of polyfluoroaromatic aldehydes, acetals and by-products.

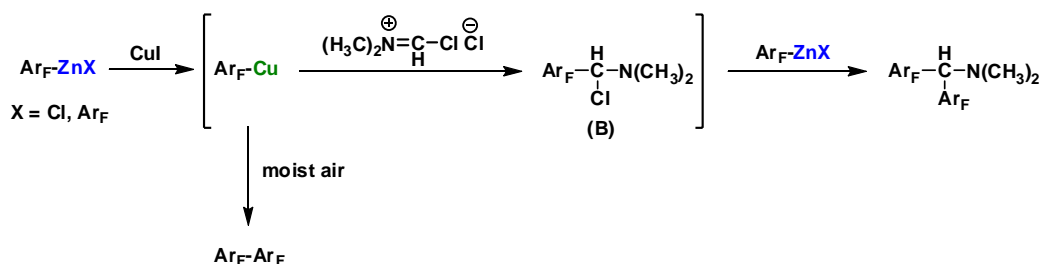
Scheme of the formation of polyfluoroaromatic aldehydes can be represented as follows (Scheme 6). Interaction of oxalyl chloride with DMF resulted in chloriminium salt (A). Vilsmeier-Haack reagent (A) reacts with polyfluoroarylcopper compounds formed from polyfluoroarylzinc reagents and copper iodide (I) to afford an intermediate compounds (B). Hydrolysis of compounds (B) or treating of the latter with methanol leads to polyfluoroaromatic aldehydes or acetals, respectively.

Scheme 6.



The formation of N,N-dimethyl-bis(polyfluoroaryl)methanamines probably occurs as a result of interaction of the intermediate compounds (B) with polyfluoroarylzinc [4] or polyfluoroarylcopper reagents. Polyfluoroaryls can be the result of oxidation of polyfluoroarylcopper compounds by moist air [5] (Scheme 7).

Scheme 7.



CONCLUSION

We have developed a new method for the synthesis of polyfluoroaromatic aldehydes and acetals, which includes the reaction of polyfluoroarylzinc compounds with Vilsmeier-Haack reagent. Acetals were prepared as a result of one-pot synthesis excluding the formation of aldehydes.

EXPERIMENTAL

NMR spectra were recorded on spectrometer Bruker AV-300 (282.4 MHz for ^{19}F and 300 MHz for ^1H) with addition $(\text{CD}_3)_2\text{CO}$ for the reaction mixture containing organozinc compounds in DMF, in other cases in CCl_4 solution. C_6F_6 (-162.9 ppm from CCl_3F) was used as the internal standards. Chemical shifts (δ) are given in ppm relative to CCl_3F and TMS. J values are in Hz. IR-spectra were registered on a Bruker Tensor 22. UV-spectra were measured on a Hewlett Packard 8453. The molecular weights and molecular formulae were determined mass-spectrometrically on a DFS high-resolution instrument (nominal ionizing electron energy 70eV). GC-MS analyses were performed with a Hewlett-Packard G1800A system consisting of an HP 5890 Series II gas chromatograph and an HP 5971 mass selective detector (HP-5 capillary column, 30 m \times 0.25 mm, stationary phase 5% of diphenyl- and 95% of dimethylpolysiloxane; carrier gas helium, flow rate 1 ml/min; injector temperature 280°C; ion source temperature 173°C, electron impact, 70 eV, a.m.u. range 30–650). GLC analyses were carried out on a Hewlett-Packard 5980 instrument equipped with an HP-5 quartz capillary column, 30 m \times 0.52 mm (stationary phase dimethyldiphenylpolysiloxane, film thickness 2.6 μm) and a thermal conductivity detector. The melting points were determined on a Kofler hot stage apparatus.

Preparation of polyfluoroarylzinc compounds.

Polyfluoroarylzinc compounds were obtained by the methods described in [2, 3].

Reaction of 1,4-dibromo-2,3,5,6-tetrafluorobenzene with Zn. The mixture of 1,4-dibromo-2,3,5,6-tetrafluorobenzene (1.86 g, 6.0 mmol), zinc dust (1.97 g 30.2 mmol), SnCl_2 (0.23 g, 1.2 mmol) and dry DMF (6 ml) was placed in closed flask and magnetically stirred under argon atmosphere at 90°C for 1 h. Then the solution of organozinc compounds was decanted from Zn and analyzed by ^{19}F NMR. According to ^{19}F NMR resulted solution contained *p*-tetrafluorophenylenedizinc bromide - 88%, 2,3,5,6-tetrafluorophenylzinc bromide - 11% and 1,2,4,5-tetrafluorobenzene - 1%.

p-Tetrafluorophenylenedizinc bromide. ^{19}F NMR, δ , ppm: 43.5 s (4F, F_{Arom}).

2,3,5,6-Tetrafluorophenylzinc bromide. ^{19}F NMR, δ , ppm: 22.6 m (2F, $F^{3,5}$), 44.7 m (2F, $F^{2,6}$).

Synthesis of polyfluoroaromatic aldehydes and acetals.

Vilsmeier-Haack reagent (general procedure). In three-necked round bottom flask equipped with a magnetic stir bar, a thermometer, a calcium chloride tube and a dropping funnel was charged with dry DMF and cooled to -15°C . To the cooled DMF a fresh distilled oxalyl chloride was slowly added. The reaction was accompanied by gas evolution and formation of white precipitate. The reaction mixture was stirred in additional 30 min at -10°C and volatile products were distilled off in vacuum (~ 2 mm Hg) for 5 min.

Pentafluorobenzaldehyde. To a solution of pentafluorophenylzinc compounds formed from chloropentafluorobenzene (40.50 g, 200 mmol), Zn dust (39.22 g, 600 mmol) and SnCl_2 (3.79 g, 20 mmol) in DMF (108 ml) CuI (7.62 g, 40 mmol) was added. The mixture was stirred under argon atmosphere to dissolve salt. The resulting solution was loaded to dropping funnel and added to Vilsmeier-Haack reagent (obtained from oxalyl chloride (38.8 g, 300 mmol) and 100 ml of dry DMF) at -10°C for 4.5 h. According to ^{19}F NMR the reaction mixture contained adduct of pentafluorophenylzinc compounds to Vilsmeier-Haack reagent – 84%, *N,N*-dimethyl-bis(pentafluorophenyl)methanamine – 10%, pentafluorobenzene – 4.5% and decafluorobiphenyl – 1.5%. The reaction mixture was poured into water and steam distilled. The organic layer was separated and dried over MgSO_4 . A mixture (29.35 g), which contained (GLC) 85.4% of pentafluorobenzaldehyde (yield 64%), 9.5% of *N,N*-dimethyl-bis(pentafluorophenyl)methanamine, 3.0% of pentafluorobenzene and 1.5% of decafluorobiphenyl (identification of the components of a mixture was performed by ^{19}F and ^1H NMR) was obtained. The distillation of this mixture in vacuum (~ 13 -14 mm Hg) gave a fraction (15.54 g) with b.p. 56 - 58°C containing (GLC) 97.8% of pentafluorobenzaldehyde, and a fraction (6.89 g) with b.p. 58 - 59°C (lit. b.p. 59 - 59.5°C / 11 mm Hg [6]) containing (GLC) 98.4% of this aldehyde. The total yield of pentafluorobenzaldehyde was 57%.

Pentafluorobenzaldehyde is colorless liquid which is slowly crystallized. IR (KBr, ν/cm^{-1}): 2930 (C-H), 2889 (C-H), 1715 (C=O) [6]. UV (*n*-hexane) $\lambda_{\text{max}}/\text{nm}$ (lg ϵ): 204 (3.67), 236 (4.05), 243 (3.99), 286 (3.20) [6]. ^1H NMR, δ : 10.23 (m, 1H, CHO) [7]. ^{19}F NMR, δ : 1.1 (m, 2F, $\text{F}^{3,5}$), 17.2-17.4 (m, 3F, F^4 and $\text{F}^{2,6}$) [8]. GC-MS: 196 (98%) [M] $^+$.

1-(Dimethoxymethyl)-2,3,4,5,6-pentafluorobenzene. The reaction of organozinc compounds formed from chloropentafluorobenzene (6.07 g, 30 mmol), Zn dust (5.55 g, 90 mmol) and SnCl_2 (0.57 g, 3 mmol) in DMF (16 ml) with Vilsmeier-Haack reagent (obtained from oxalyl chloride (6.09 g, 48 mmol) and 15 ml of dry DMF) in the presence of CuI (1.14 g, 6 mmol) was performed. To the reaction mixture methanol (25 ml) was added and resulting solution was heated at 65 - 70°C for 13.5 h. Then the reaction mixture was poured into water and steam distilled. The organic layer was separated, dried over MgSO_4 and distilled in vacuum (~ 3 mm Hg). A fraction (2.24 g) boiling

at 47-48°C is collected. This fraction contained (GLC) 97% of 1-(dimethoxymethyl)-2,3,4,5,6-pentafluorobenzene (yield 31%).

1-(Dimethoxymethyl)-2,3,4,5,6-pentafluorobenzene is colorless liquid. ^1H NMR, δ : 3.40 (s, 6H, CH_3), 5.54 (s, 1H, CH) [9]. ^{19}F NMR, δ : -0.3 (m, 2F, $\text{F}^{3,5}$), 7.8 (t.t, 1F, F^4 , $J = 20$, $J = 2$), 20.5 (m, 2F, $\text{F}^{2,6}$) [9]. GC-MS: 242 $[\text{M}]^+$.

2,3,5,6-Tetrafluoro-4-(trifluoromethyl)benzaldehyde. To a solution of 4-(trifluoromethyl)-2,3,5,6-tetrafluorophenylzinc compounds formed from octafluorotoluene (11.80 g, 50 mmol), Zn dust (9.81 g, 150 mmol) and SnCl_2 (0.95 g, 5 mmol) in DMF (27 ml) CuI (1.90 g, 10 mmol) was added. The mixture was stirred under argon atmosphere to dissolve salt. The resulting solution was loaded to dropping funnel and added to Vilsmeier-Haack reagent (obtained from oxalyl (10.15 g, 80 mmol) chloride and 25 ml of dry DMF) at -10°C for 2.5 h. According to ^{19}F NMR the reaction mixture contained an adduct of organozinc compounds to Vilsmeier-Haack reagent – 90%, *N,N*-dimethyl-bis[4-(trifluoromethyl)-2,3,5,6-tetrafluorophenyl]methanamine – 4%, 1,2,4,5-tetrafluoro-3-(trifluoromethyl)benzene – 4% and 4,4'-bis(trifluoromethyl)octafluorobiphenyl – 2%. The reaction mixture was poured into water and steam distilled. The organic layer was separated and dried over MgSO_4 . A mixture (9.94 g) contained (GLC) 84.7% of 2,3,5,6-tetrafluoro-4-(trifluoromethyl)benzaldehyde (yield 69%), 9.1% of *N,N*-dimethyl-bis[4-(trifluoromethyl)-2,3,5,6-tetrafluorophenyl]methanamine, 2.6% of 1,2,4,5-tetrafluoro-3-(trifluoromethyl)benzene and 2.6% of 4,4'-bis(trifluoromethyl)octafluorobiphenyl. The mixture is distilled in vacuum (~ 14 -15 mm Hg) and a fraction (6.39 g) boiling at 66-70°C (lit. b.p. $52^\circ\text{C} / 2$ mm Hg [10]) contained (GLC) 99% of 2,3,5,6-tetrafluoro-4-(trifluoromethyl)benzaldehyde (yield 52%) is collected.

2,3,5,6-Tetrafluoro-4-(trifluoromethyl)benzaldehyde is colorless solid, m.p. 27 - 30°C . IR (CCl_4 , ν/cm^{-1}): 2882 (C-H), 1719 (C=O) [10]. UV (*n*-hexane) $\lambda_{\text{max}}/\text{nm}$ ($\lg \epsilon$): 206 (3.82), 231 (4.04), 238 (3.97), 304 (3.32). ^1H NMR, δ : 10.32 (s, 1H, CHO) [10]. ^{19}F NMR, δ : 18.6 (m, 2F, $\text{F}^{2,6}$), 22.6 (m, 2F, $\text{F}^{3,5}$), 105.1 (t, 3F, CF_3 , $J = 22$) [10]. GC-MS: 246 (98%) $[\text{M}]^+$.

1-(Dimethoxymethyl)-4-(trifluoromethyl)-2,3,5,6-tetrafluorobenzene. To the reaction mixture prepared as described above a methanol (25 ml) was added and resulting solution was heated at 65 - 70°C for 7 h. After the reaction mixture was poured into water and steam distilled. The solid organic layer was extracted CH_2Cl_2 (3x40 ml) and dried over MgSO_4 . The solvent was distilled off in vacuum to give a mixture (8.2 g) contained (^{19}F and ^1H NMR) 47% of 1-(dimethoxymethyl)-4-(trifluoromethyl)-2,3,5,6-tetrafluorobenzene (yield 21%).

2,3,5,6-Tetrafluoro-4-formylbenzotrile. To a solution of 4-cyano-2,3,5,6-tetrafluorophenylzinc compounds formed from pentafluorobenzotrile (9.65 g, 50 mmol), Zn dust (9.81 g, 150 mmol) and SnCl_2 (0.95 g, 5 mmol) in DMF (27 ml) CuI (1.90 g, 10 mmol) was added. The mixture was stirred under argon atmosphere to dissolve salt. The resulting solution was loaded

to dropping funnel and added to Vilsmeier-Haack reagent (obtained from oxalyl chloride (10.15 g, 80 mmol) and 25 ml of dry DMF) at -10°C for 1.5 h. According to ¹⁹F NMR the reaction mixture contained an adduct of organozinc compounds to Vilsmeier-Haack reagent – 81%, N,N-dimethyl-bis(4-cyano-2,3,5,6-tetrafluorophenyl)methanamine – 6%, 2,3,5,6-tetrafluorobenzonitrile – 11% and 4,4'-bis(cyano)octafluorobiphenyl – 2%. The reaction mixture was poured into water (150 ml) and extracted with CH₂Cl₂ (3x40 ml), washed with water (100 ml). The organic layer was separated and dried over MgSO₄. The solvent was distilled off in vacuum and water (100 ml) was added to residue to give brown solid. This solid was filtered off to give 6.88 g of a product contained (¹⁹F and ¹H NMR) 77% of 2,3,5,6-tetrafluoro-4-formylbenzonitrile (yield 52%). After column chromatography on silica gel (70-230 mesh, CHCl₃ as an eluent) of this product (2.5 g) 1.42 g of 2,3,5,6-tetrafluoro-4-formylbenzonitrile was isolated.

2,3,5,6-Tetrafluoro-4-formylbenzonitrile is colorless crystalline substance (plates), m.p. 105-106°C (*n*-hexane). IR (KBr, ν/cm^{-1}): 2938 (C-H), 2911 (C-H), 2253 (C≡N), 1701 (C=O), 1654, 1491, 1420, 1395, 1310, 1266, 1089, 997, 909, 807, 629, 492. UV (EtOH) $\lambda_{\text{max}}/\text{nm}$ (lg ϵ): 201 (3.97), 228 (4.08), 235 (4.08), 292 (3.31). ¹H NMR, δ : 10.31 (s, 1H, CHO). ¹⁹F NMR, δ : 19.0 (m, 2F, F^{3,5}), 30.1 (m, 2F, F^{2,6}). MS, (EI, m/z (rel.%)): 203 (95) [M]⁺, 202 (100) [M – H]⁺, 175 (41) [M – CO]⁺, 174 (31) [M – CHO]⁺, 148 (8) [C₆F₄]⁺, 124 (40), 106 (17), 105 (11), 29 (14) [CHO]⁺, 28 (14) [CO]⁺. HRMS, calculated for C₈HF₄NO: 202.9989; found: 202.9985.

1,1,2,2,3,3,4,6,7-Nonafluoro-2,3-dihydro-1H-indene-5-carbaldehyde. To solution of organozinc compounds formed from perfluoroindan (14.90 g, 50 mmol), Zn dust (9.81 g, 150 mmol) and SnCl₂ (0.95 g, 5 mmol) in DMF (27 ml) CuI (1.90 g, 10 mmol) was added. The mixture was stirred under argon atmosphere to dissolve salt. The resulting solution was loaded to dropping funnel and added to Vilsmeier-Haack reagent (obtained from oxalyl chloride (10.15 g, 80 mmol) and 25 ml of dry DMF) at -10°C for 2.5 h. According to ¹⁹F NMR the reaction mixture contained an adduct of organozinc compounds to Vilsmeier-Haack reagent – 76%, N,N-dimethyl-bis(nonafluoroindan-5-yl)methanamine – 12%, 1,1,2,2,3,3,4,6,7-nonafluoroindan – 9% and perfluorobiindanyl – 3%. The reaction mixture was poured into water and steam distilled. The organic layer was separated and dried over MgSO₄. A mixture (9.97 g), which contained (GLC) 78.1% of 1,1,2,2,3,3,4,6,7-nonafluoro-2,3-dihydro-1H-indene-5-carbaldehyde (yield 51%), 8.6% of 1,1,2,2,3,3,4,6,7-nonafluoroindan, 3.0% of perfluorobiindanyl was obtained. The distillation of this mixture in vacuum (~4 mm Hg) gave a fraction (6.24 g) boiling at 63-68°C, which contained (GLC) 96% of 1,1,2,2,3,3,4,6,7-nonafluoro-2,3-dihydro-1H-indene-5-carbaldehyde (yield 39%).

1,1,2,2,3,3,4,6,7-Nonafluoro-2,3-dihydro-1H-indene-5-carbaldehyde is a light yellow crystalline substance, m.p 120-122°C. IR (CCl₄, ν/cm^{-1}): 2879 (C-H), 1722 (C=O), 1649, 1499, 1460, 1383, 1331, 1256, 1205, 1163, 1099, 1040, 999, 941. UV (*n*-hexane) $\lambda_{\text{max}}/\text{nm}$ (lg ϵ): 206

(3.59), 232 (3.22), 278 (2.75). ^1H NMR, δ : 10.35 (s, 1H, CHO). ^{19}F NMR, δ : 21.5 (t.t, 1F, F^7 , $J = 21$, $J = 7.5$), 31.8 (quint, 4F, F^2 , $J = 4.5$), 35.4 (d.m, 1F, F^6 , $J = 20.5$), 42.5 (d.q, 1F, F^4 , $J = 22$, $J = 7.3$), 53.7 and 54.8 (both m, 2F, F^1 and F^3 MS, (EI, m/z (rel.%)): 308 (53) $[\text{M}]^+$, 307 (100) $[\text{M} - \text{H}]^+$, 279 (5) $[\text{M} - \text{CHO}]^+$, 29 (4) $[\text{CHO}]^+$. HRMS, calculated for $\text{C}_{10}\text{HF}_9\text{O}$: 307.9878; found: 307.9872.

2,3,5,6-Tetrafluoropyridine-4-carbaldehyde. To solution of organozinc compounds formed from pentafluoropyridine (8.45 g, 50 mmol), Zn dust (9.81 g, 150 mmol) and SnCl_2 (0.95 g, 5 mmol) in DMF (27 ml) CuI (1.90 g, 10 mmol) was added. The mixture was stirred under argon atmosphere to dissolve salt. The resulting solution was loaded to dropping funnel and added to Vilsmeier-Haack reagent (obtained from oxalyl chloride (19.04 g, 150 mmol) and 25 ml of dry DMF) at -10°C for 2 h. According to ^{19}F NMR the reaction mixture contained an adduct of organozinc compounds to Vilsmeier-Haack reagent – 77.5%, *N,N*-dimethyl-bis(2,3,5,6-tetrafluoropyridin-4-yl)methanamine – 7%, 2,3,5,6-tetrafluoropyridine – 11%, 4,4'-octafluorobipyridyl – 4.5%. The reaction mixture was poured into water (150 ml) and extracted with CHCl_3 (3x50 ml), washed with water (100 ml). The organic layer was separated and dried over MgSO_4 . The solvent was removed under reduced pressure and the residue was distilled in vacuum ($\sim 18\text{-}20$ mm Hg). A fraction (5.53 g) boiling at $47\text{-}51^\circ\text{C}$ (lit. b.p. $52\text{-}54^\circ\text{C}$ / 20 mm Hg [11]) contained (GLC) 68% of 2,3,5,6-tetrafluoropyridine-4-carbaldehyde (yield 42%) is collected.

2,3,5,6-Tetrafluoropyridine-4-carbaldehyde is colorless liquid. ^1H NMR, δ : 10.28 (s, 1H, CHO). ^{19}F NMR, δ : 15.7 (m, 2F, $F^{3,5}$), 73.1 (m, 2F, $F^{2,6}$) [11].

Tetrafluoroterephthalaldehyde. To a solution of organozinc compounds formed from 1,4-dibromo-2,3,5,6-tetrafluorobenzene (1.86 g, 6.0 mmol), zinc dust (1.97 g 30.2 mmol), SnCl_2 (0.23 g, 1.2 mmol) and dry DMF (6 ml) CuI (0.23 g, 1.208 mmol) was added. The mixture was stirred under argon atmosphere to dissolve salt. The resulting solution was loaded to dropping funnel and added to Vilsmeier-Haack reagent (obtained from oxalyl chloride (3.07 g, 24.16 mmol) and 4 ml of dry DMF) at -10°C for 1 h. The reaction mixture was poured into water (150 ml) and extracted with CHCl_3 (3x40 ml), washed with water (100 ml). The organic layer was separated and dried over MgSO_4 . According to GC-MS extract contained mainly tetrafluoroterephthalaldehyde (GC-MS: $[\text{M}]^+ = 206$) and 2,3,5,6-tetrafluorobenzaldehyde (GC-MS: $[\text{M}]^+ = 178$). After removal of solvent the residue (brown solid, 0.33 g) was purified by sublimation ($110\text{-}115^\circ\text{C}$, ~ 4 mm Hg) to give 0.16 g of tetrafluoroterephthalaldehyde (yield 13%).

Tetrafluoroterephthalaldehyde is a colorless crystalline substance (needles), m.p. $127\text{-}128^\circ\text{C}$ (chloroform) (lit. m.p. $130\text{-}132^\circ\text{C}$ [12]). ^1H NMR, δ : 10.31 (s, 1H, CHO) [12]. ^{19}F NMR, δ : 17.2 (s, 4F) [12].

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