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# Preparation of heptafluoronaphthyllithiums and -magnesiums: An unexpected difference in the reactivity of isomers $C_{10}F_7H$ and $C_{10}F_7Br$ towards organolithium and organomagnesium compounds

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## ABSTRACT

Significant differences in the reactivity of isomeric heptafluoronaphthalenes and bromoheptafluoronaphthalenes towards organolithium and organomagnesium compounds were found. Metalation of polyfluorinated naphthalenes 2-$C_{10}F_7X$ (X = H, Br) occurs easily under the action of bases (BuLi, *t*-BuLi, LDA) as well as EtMgBr (X = Br) in ether. This fact was proven by $^{19}F$ NMR spectroscopy and by trapping of 2-$C_{10}F_7M$ (M = Li, MgBr, Mg(2-$C_{10}F_7$)) with electrophile $ClSiMe_3$. The interaction of 1-$C_{10}F_7Br$ with BuLi or EtMgBr proceeds in a similar way. In contrast to 2-$C_{10}F_7H$, isomeric 1-$C_{10}F_7H$ is the less acidic substrate and undergoes only the nucleophilic alkyldefluorination when combined with BuLi or *t*-BuLi.

## 1. Introduction

Polyfluoroaromatic derivatives of lithium and magnesium were intensively investigated in 1960–1980s. Preparation and main properties of $Ar_FM$ (M = Li, MgX) are well known, and these reagents are employed in routine synthesis of organic and organometallic compounds [1–3]. Surprisingly, there is only scarce literary information about preparation of the polyfluoronaphthyllithium and magnesium derivatives. The initial communication on the preparation of $C_{10}F_7MgCl$ from $C_{10}F_7Cl$ (isomer mixture) and Mg pre-activated with 1,2-dibromoethane (DBE) in ether followed by hydrolysis to $C_{10}F_7H$ was reported by a Russian team in 1964 [4]. A solution of 1-$C_{10}F_7MgBr$ was prepared the same way from 1-$C_{10}F_7Br$ and after substitution of THF for ether the Grignard reagent was carboxylated with $CO_2$ to give 1-$C_{10}F_7COOH$ at 50% yield [5]. Reflux of 2-$C_{10}F_7Br$ and magnesium pre-activated with DBE in ether leads to the formation of 2-$C_{10}F_7MgBr$ and the latter reacts with N-methylformanilide to yield 2-$C_{10}F_7CHO$ (72%) [6]. Metalation of 1-bromo-3,4,5,6,7,8-hexafluoronaphthalene with *i*-PrMgCl in THF at room temperature gives the corresponding polyfluorinated naphthylmagnesium halide and the further reaction with $CuBr{\cdot}SMe_2$ produces 2,2′-dihydryldodecafluoro-1,1′-binaphthyl at 86% yield [7]. *Respess* and *Tamborski* prepared “organometallic solution” from octafluoronaphthalene and ethylmagnesium bromide in THF using anhydrous $CoCl_2$ as the catalyst. Hydrolysis of the “organometallic solution” gave 2-H-heptafluoronaphthalene (for convenience, the hydrogen atom is designated as a substituent H) at a moderate yield [8]. The action of BuLi on 2-$C_{10}F_7Br$ in hexane at −30 °C followed by treatment of the resulting 2-heptafluoronaphthyllithium with boron trichloride gives tris(heptafluoro-2-naphthyl)boron in 26% yield [9]. Metalation of 2-H-heptafluoronaphthalene with BuLi in ether – hexane at −75 °C was also described [10,11]. Carboxylation of the formed 2-$C_{10}F_7Li$ gives 2-$C_{10}F_7COOH$ (60%), whereas the reaction with bromine leads to 2-$C_{10}F_7Br$ and 2-$C_{10}F_7H$ (5:1). Thermal decomposition of 2-$C_{10}F_7Li$ in ether results in hexafluoro-1,2-naphthalyne, the latter being trapped with furan to form 1,4-epoxy-5,6,7,8,9,10-

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hexafluoro-1,4-dihydrophenanthrene. It should be noted that the generation of polyfluoronaphthylmetal derivatives was assumed from their chemical reactions but these intermediates were not observed directly.

The study was aimed at preparation of polyfluorinated naphthyl derivatives of some elements using $C_{10}F_7M$ as nucleophiles. Preliminary experiments showed the satisfactory results with 2-heptafluoronaphthyllithium and unexpected difficulties with the 1-naphthyl isomer. This prompted us to investigate the metalation reactions of 1-H-heptafluoronaphthalene (**1**), 2-H-heptafluoronaphthalene (**2**), 1-bromoheptafluoronaphthalene (**3**) and 2-bromoheptafluoronaphthalene (**4**) with butyllithium, *t*-butyllithium, LDA and ethylmagnesium bromide with the aim of developing a reliable procedure for the generating of the corresponding naphthylmetals.

## 2. Results and discussion

Although naphthalenes **1**, **2**, **3** and **4** are known compounds, practical routes to 1-$C_{10}F_7H$ and 1-$C_{10}F_7Br$ are not convenient. There are no literature data about synthesis of naphthalene **1** but only decarboxylation of 1-$C_{10}F_7COOH$ [5]. Individual naphthalenes **1** and **2** were obtained by vacuum rectification of their mixture prepared by hydrolysis of the corresponding organomagnesium compounds obtained from a mixture of isomeric $C_{10}F_7Cl$ (Scheme 1). It should be pointed out that all attempts to separate directly the mixture of $C_{10}F_7Cl$ failed.

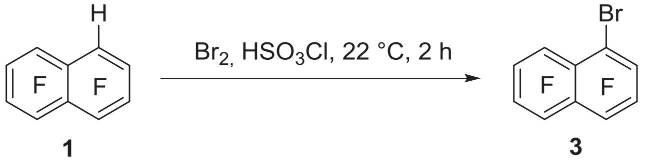
It is important to note that the initial mixture consisted of 1-$C_{10}F_7Cl$ and 2-$C_{10}F_7Cl$ in molar ratio 1:1.5. After hydrolysis, conversions of 1-$C_{10}F_7Cl$ and 2-$C_{10}F_7Cl$ were 84 and 95%, respectively. Perhaps, this is a consequence of the higher metalation rate of the latter isomer. In the past, the predominant formation of 2-$C_{10}F_7COOH$ from $C_{10}F_7Cl$, Mg and $CO_2$ was explained by the lower reactivity of 1-$C_{10}F_7MgCl$ towards the electrophile [5] but the lower reactivity of 1-$C_{10}F_7Cl$ towards magnesium also contributes to the process.

To our knowledge, the only reported route to naphthalene **3** is bromination of **1** with $Br_2$ in the presence of iron filings (20 °C, 2 h) [5]. An attempted reproduction gave **3** contaminated with 1,5-dibromohexafluoronaphthalene (up to 15–20%) which could not be removed by recrystallization as well as by sublimation. The desirable compound was obtained by bromination of **1** with bromine in $HSO_3Cl$ (Scheme 2).

Although the formation of $C_6F_5MgBr$ from $C_6F_5H$ and EtMgBr in THF [8,12] was described, both $C_6F_5H$ and isomers $C_{10}F_7H$ do not react with EtMgBr in ether (22 °C, 3–5 h). The stronger Lewis base, butyllithium, metalates **2** in ether-hexane at low temperature and formed 2-$C_{10}F_7Li$ was trapped with chlorotrimethylsilane to yield 2-trimethylsilylheptafluoronaphthalene (**5**) that coincides with the literature data mentioned above. The similar process occurs in the case of **2** and *t*-BuLi or LDA (Scheme 3).

2-Heptafluoronaphthyllithium was also prepared by metal-bromine exchange from 2-bromoheptafluoronaphthalene and BuLi and reacted with $ClSiMe_3$ giving **5** (Scheme 4).

In contrast to 2-$C_{10}F_7H$, the reaction of 1-$C_{10}F_7H$ with BuLi at $-65 \div -70$ °C and the subsequent treatment with $ClSiMe_3$ does not give 1-trimethylsilylheptafluoronaphthalene (**6**). 1-H-3-butylhexafluoronaphthalene (**7**), 1-H-6-butylhexafluoronaphthalene (**8**), 1-H-7-butylhexafluoronaphthalene (**9**), 1-H-3,7-dibutylpentafluoronaphthalene (**10**) and **1** (trace) formed (GSMS, $^{19}F$ NMR) instead of **6** (Scheme 5). The same products also are obtained by the reaction of **1** with BuLi at −80 °C without addition of $ClSiMe_3$ but in this case the conversion of **1** is less than that in the previous case because of the lower temperature and shorter deprotonation time (15 min instead of 3 h) before $ClSiMe_3$ treatment.



**Scheme 2.** Preparation of 1-bromoheptafluoronaphthalene.

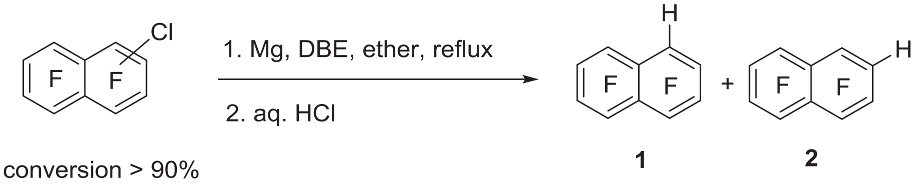
Using more basic and less nucleophilic *t*-BuLi instead of BuLi does not affect the final result and nucleophilic substitution of fluorine atoms remains the only reaction way. According to GCMS and $^{19}F$ NMR data the reaction mixture contains **1**, 1-H-*t*-butylhexafluoronaphthalenes **11**, **12**, and **13**, 1-H-di(*t*-butyl)pentafluoronaphthalenes **14** and **15** along with minor admixtures (presumably, 1-H-tri(*t*-butyl)tetrafluoronaphthalenes) (Scheme 6).

LDA was used as the base to avoid the nucleophilic substitution. However, neither metalation nor nucleophilic substitution occurred (Scheme 7).

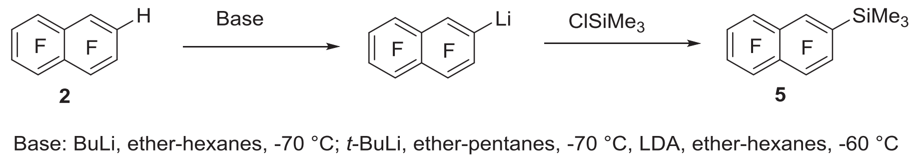
These results demonstrate that 1-$C_{10}F_7H$ is far less acidic than its isomer 2-$C_{10}F_7H$ and, therefore, competitive nucleophilic alkyldefluorination of **1** with alkyllithium occurs rather than metalation. This assumption was confirmed by the reaction of **1** with one equivalent of BuLi at lower temperature (−80°C). The reaction yielded the same compounds **7**, **8**, and **9** at a decreased conversion of **1**. However, the fast formation of 1-$C_{10}F_7Li$ followed by substitution in the latter is not excluded because hydrolysis of the reaction mixture would give the same products. Thus, this assumption was used for the explanation of the interaction between 2-$C_{10}F_7Br$ and BuLi [10].

Metalation of $Ar_FBr$ with BuLi is known to proceed much faster than $Ar_FH$ metalation under identical conditions [13]. We conducted the reaction of 1-$C_{10}F_7Br$ with a deficient quantity of BuLi at −80 °C. After hydrolysis of the reaction mixture at this temperature we obtained **1** and **3** whereas the products of nucleophilic alkylation were not detected. This means that the lithium-bromine exchange in 1-$C_{10}F_7Br$ at −80 °C is the fast process and 1-$C_{10}F_7Li$ does not react with BuLi. The second consequence is an exclusion of 1-$C_{10}F_7Li$ as a reactive intermediate in Schemes 5 and 6. The formation of 1-$C_{10}F_7Li$ is proved by the conversion of **3** to 1-trimethylsilylheptafluoronaphtalene (**6**) *via* organolithium trapping with $ClSiMe_3$ (Scheme 8).

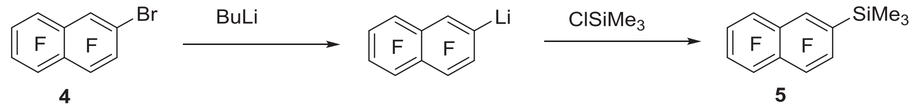
Heptafluoronaphthylmagnesiums were prepared in two ways:



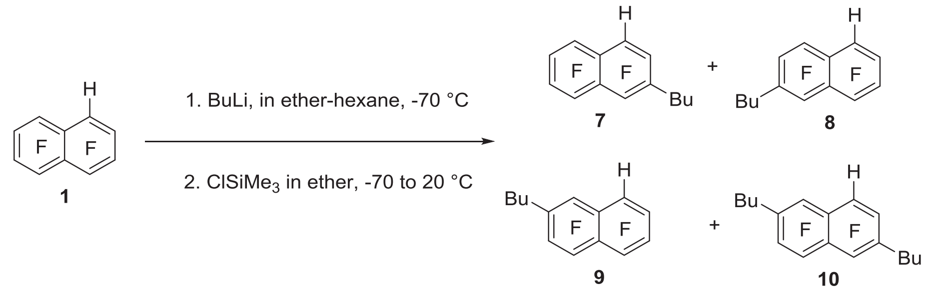
**Scheme 1.** Preparation of heptafluoronaphthalenes from chloroheptafluoronaphthalenes.



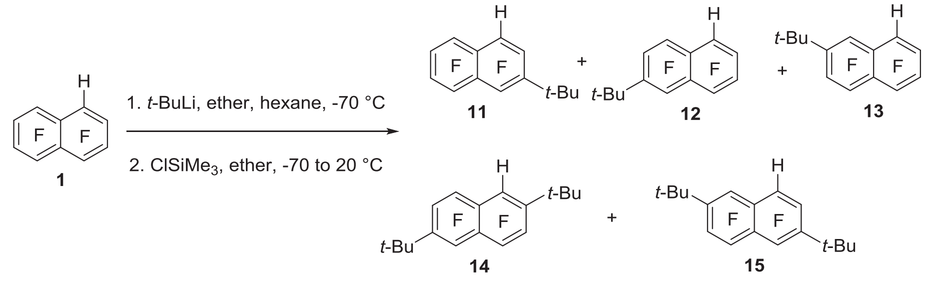
**Scheme 3.** Generation of 2-$C_{10}F_7Li$ from **2** and trapping with $CiSiMe_3$.



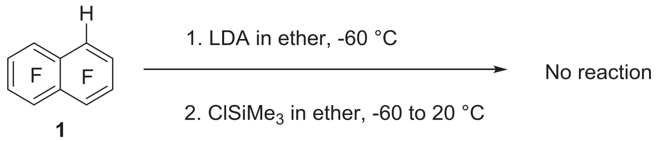
**Scheme 4.** Generation of 2-$C_{10}F_7Li$ from **4** and trapping with $ClSiMe_3$.



**Scheme 5.** Attempted generation of 1-$C_{10}F_7Li$ from **1** and BuLi.



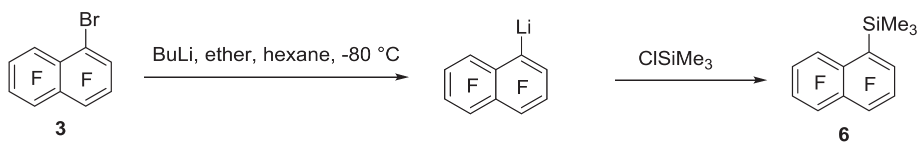
**Scheme 6.** Attempted generation of 1-$C_{10}F_7Li$ from **1** and t-BuLi.



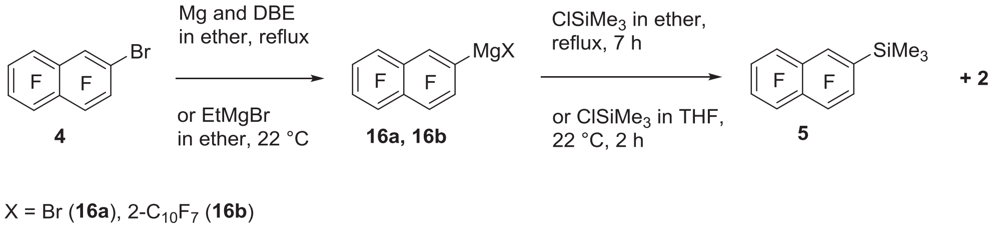
**Scheme 7.** Failed generation of 1-$C_{10}F_7Li$ from **1** and LDA.

by the reaction of $C_{10}F_7Br$ with magnesium and metal-bromine exchange with EtMgBr. The formation of 2-heptafluoronaphthylmagnesium bromide (**16a**), bis(2-heptafluoronaphthyl)magnesium (**16b**), **2** and the residual amount of **4** was detected by $^{19}$F NMR when the ethereal solution of 2-bromoheptafluoronaphthalene was refluxed with excess magnesium turnings pre-activated with DBE (0.3 equiv.) for 2 h. The total consumption of **4** was observed in 6 h of refluxing. Changing magnesium turnings to powder did not affect the results of the reaction. Refluxing naphthylmagnesiums **16a** and **16b** with $ClSiMe_3$ for 2 h did not result in the formation of **5**, and exhaustive silylation was only observed in 7 h.

Alternatively, naphthylmagnesiums **16a** and **16b** were observed after addition of **4** to ethylmagnesium bromide in ether. Because the reaction of **16a** and **16b** with $ClSiMe_3$ in ether proceeded slowly, we performed it in a mixture of ether and THF. This allowed us to



**Scheme 8.** Formation of 1-$C_{10}F_7Li$ from **3** and BuLi and reaction with $ClSiMe_3$.



**Scheme 9.** Formation of 2-heptafluoronaphthylmagnesiums **16a** and **16b** and their conversion to **5**.

get the product **5** at 78% yield after stirring at 22 °C for 2 h (Scheme 9).

It is important that the quantity of **2** was always significant despite the precautions against moisture. This extreme hydrolysis may be the reason for “moderate” yields of products obtained *via* nucleophile 2-$C_{10}F_7MgX$ [5,6,8]. Meanwhile, pentafluorophenylmagnesiums had the similar reactivity towards $ClSiMe_3$ and stirring of $C_6F_5MgX$ with this electrophile in ether at 22°C for 4 h results in a mixture of $C_6F_5MgX$, $C_6F_5H$ and $C_6F_5SiMe_3$, the latter being a minor component.

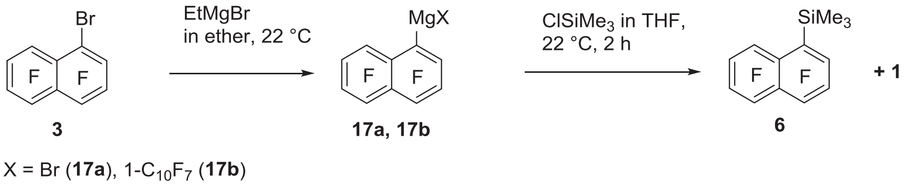
Similar to the reaction of **4** with Mg, the generation of 1-heptafluoronaphthylmagnesiums from **3** and magnesium in ether required more than 1 equivalent of DBE. Thus, addition of **3** and DBE (0.4 equiv.) to magnesium (1.5 equiv.) in ether, heating at 36–40 °C and subsequent hydrolysis of the solution led to the mixture of **3** and **1** (2:1) due to the incomplete metalation. Alternatively, addition of **3** (1 equiv.) and DBE (1.4 equiv.) to magnesium (3 equiv.) gave small amounts of **3** and **1** and only one 1-heptafluoronaphthylmagnesium derivative (**17b**). In the $^{19}F$ NMR spectrum of the latter, there were equally intensive signals at −106.90, −142.2, −146.1, −148.3, −159.3, −161.5 and −161.6 ppm. The spin-spin coupling analysis allowed us to assign the signals to fluorine atoms $F^2$, $F^8$, $F^4$, $F^5$, $F^3$, $F^6$, and $F^7$, respectively.

Another picture was obtained when **3** reacted with EtMgBr. In addition to above signals, the $^{19}F$ NMR spectrum contained broad resonances ($\omega_{½}$ ~ 100–110 Hz) at −106.80 and −143.0 ppm and signals at −145.9 ($F^4$), −148.1 ($F^5$), −159.2 ($F^3$), −161.4 and −161.6 ($F^6$ and $F^7$) ppm. Signals of fluorine atoms $F^5$, $F^3$, and $F^6$ of this naphthylmagnesium (**17a**) interfered with signals of **17b**. Assuming that the signals broadening at −106.80 and −143.0 ppm was due to the exchange with the Grignard reagent, the amount of the latter was reduced to 0.8 equivalent. But this did not affect the width of the signals.

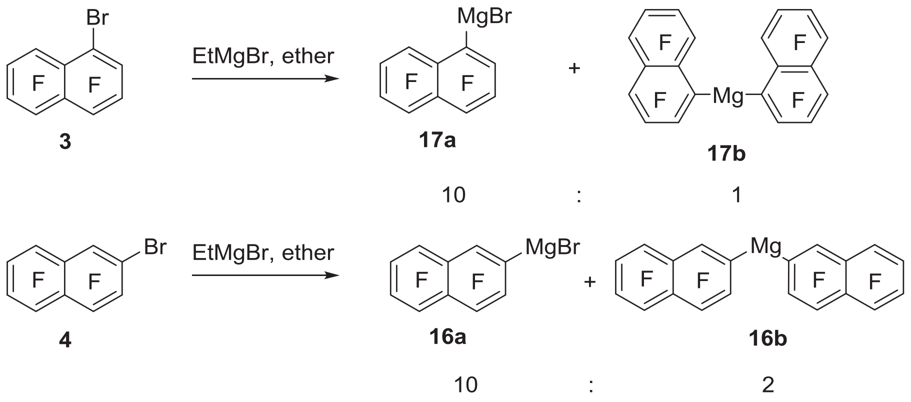
Besides $^{19}F$ NMR data, the formation of 1-naphthylmagnesium compounds **17a** and **17b** was proved by their conversion to 1-trimethylsilylheptafluoronaphthalene **6** by the reaction with $ClSiMe_3$ in THF at 22°C. Similar to 2-heptafluoronaphthylmagnesiums, 1-$C_{10}F_7MgX$ (X = Br, 1-$C_{10}F_7$) were very sensitive to moisture and manipulations with their solutions often led to partial hydrolysis (Scheme 10).

Metalation of individual bromoheptafluoronaphthalenes with EtMgBr demonstrates the same equilibrium positions $Ar_FMgBr/(Ar_F)_2Mg$ as described above. Thus, the molar ratio of 1-heptafluoronaphthylmagnesium bromide (**17a**) to bis(1-heptafluoronaphthyl)magnesium (**17b**) was 10:1. The molar ratio of 2-heptafluoronaphthylmagnesium bromide (**16a**) to bis(2-heptafluoronaphthyl)magnesium (**16b**) was 10:2 in the range of concentrations 0.12–0.23 M. This fact can be accounted for by a less steric hindrance in **16b** than in **17b** (Scheme 11).

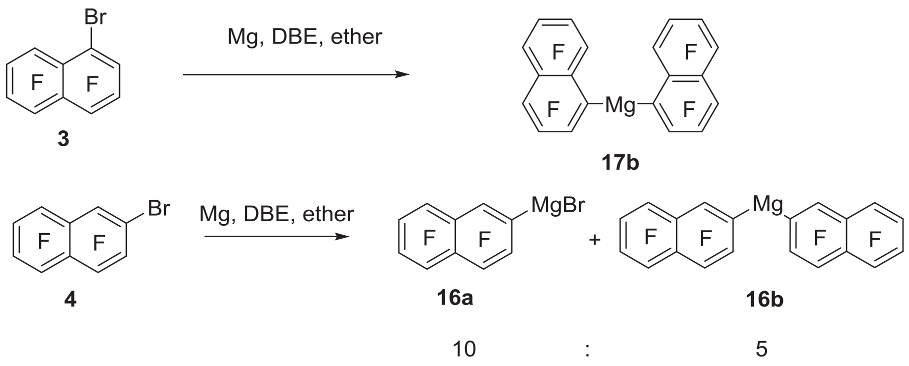
When naphthylmagnesiums 2-$C_{10}F_7MgX$ and (2-$C_{10}F_7)_2Mg$



**Scheme 10.** Formation of 1-naphthylmagnesiums **17a**, **17b** from **3** and reaction with $ClSiMe_3$.



**Scheme 11.** Formation of heptafluoronaphthylmagnesiums from bromoheptafluoronaphthalenes and EtMgBr.



**Scheme 12.** Formation of heptafluoronaphthylmagnesiums from bromoheptafluoronaphthalenes and Mg.

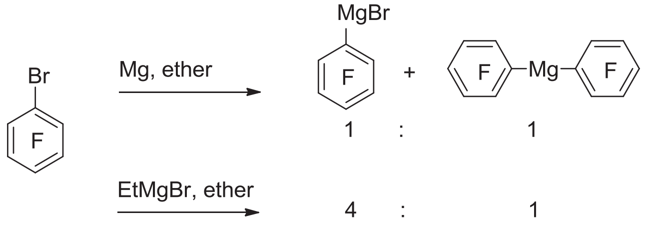
were obtained from **4** and Mg, the ratio **16a**:**16b** was 10:5, i.e. the contribution of **16b** increased (Scheme 12). Metalation of **3** with Mg seems to be the extreme case because of the formation of only **17b**. Comparing the equilibrium ratios $Ar_FMgBr/(Ar_F)_2Mg$ obtained by the reaction of $Ar_FBr$ with EtMgBr or with Mg we observed enrichment with $(Ar_F)_2Mg$ for as yet unknown reason. Moreover, this contradicts to expected change of equilibrium because the accompanying reaction of magnesium with DBE leads to the formation of $MgBr_2$, and the accumulation of the latter should lead to a shift of equilibrium to the left.

The Schlenk equilibrium in the series of $C_6F_5MgHal$ and related arylmagnesiums was studied by the $^{19}F$ NMR spectroscopy [14]. $C_6F_5MgHal$ were prepared from aryl halide and magnesium, and symmetric $(C_6F_5)_2Mg \cdot OEt_2$ was obtained by metathesis of $C_6F_5HgMe$ with $Et_2Mg$. The equilibrium ratio of $C_6F_5MgHal$ to $(C_6F_5)_2Mg$ in ether was 2.0, 1.0 and 1.4 at Hal = Cl, Br and I, respectively. When we combined solutions of $C_6F_5Br$ and EtMgBr (1:1 mol) at 22°C, the other proportion $C_6F_5MgBr:(C_6F_5)_2Mg = 4:1$ was observed (Scheme 13).

In studying the Schlenk equilibrium ($^{19}F$ NMR), arylmagnesium bromides $Ar_FMgBr$ were found to predominate in the solution obtained by the reaction of EtMgBr with the equimolar mixture of $C_6F_5Br$ with each of $C_{10}F_7Br$ isomers (Scheme 14). In addition, there were observed signals of $C_{10}F_7MgC_6F_5$. The constitutions of them were outlined from the closed similarity of chemical shifts to those of the related arylmagnesiums $C_{10}F_7MgX$ (X = Br, $C_{10}F_7$) and $C_6F_5MgY$ (Y = Br, $C_6F_5$) and the equal intensities of the $C_{10}F_7$ and $C_6F_5$ moieties resonances (Scheme 14).

## 3. Conclusions

2-H-Heptafluoronaphthalene has the sufficient acidity to form 2-$C_{10}F_7Li$ under the action of BuLi, *t*-BuLi and LDA in ether. Acidity of 1-$C_{10}F_7H$ is much lower and the above bases are ineffective in the formation of 1-$C_{10}F_7Li$. Oppositely, the nucleophilic alkyldefluorination proceeds even below −70°C. Both isomers $C_{10}F_7Br$ undergo the bromine-lithium exchange with BuLi in ether to give the corresponding $C_{10}F_7Li$. Successful metalation of $C_{10}F_7Br$ with magnesium in ether requires the use of ≥1 equivalent of dibromoethane (the accompanying reaction). Alternatively, metalation of $C_{10}F_7Br$ with EtMgBr occurs easily at 22°C. The equilibrium ratio $Ar_FMgBr/(Ar_F)_2Mg$ ($Ar_F$ = 1-$C_{10}F_7$, 2-$C_{10}F_7$, $C_6F_5$) in ether is 10:(1−2.5) when $Ar_FMgX$ is obtained from $Ar_FBr$ and EtMgBr. The contribution of $(Ar_F)_2Mg$ increases dramatically when $Ar_FMgX$ is obtained from $Ar_FBr$ and magnesium and it achieves 0:10 at $Ar_F$ = 1-$C_{10}F_7$. The rate of chlorine nucleophilic substitution in $ClSiMe_3$ with $C_{10}F_7MgX$ is low at the room temperature in ether but increases in the presence of THF.



**Scheme 13.** Ratio of $C_6F_5MgBr$ and $(C_6F_5)_2Mg$ in ether obtained by different ways.

## 4. Experimental

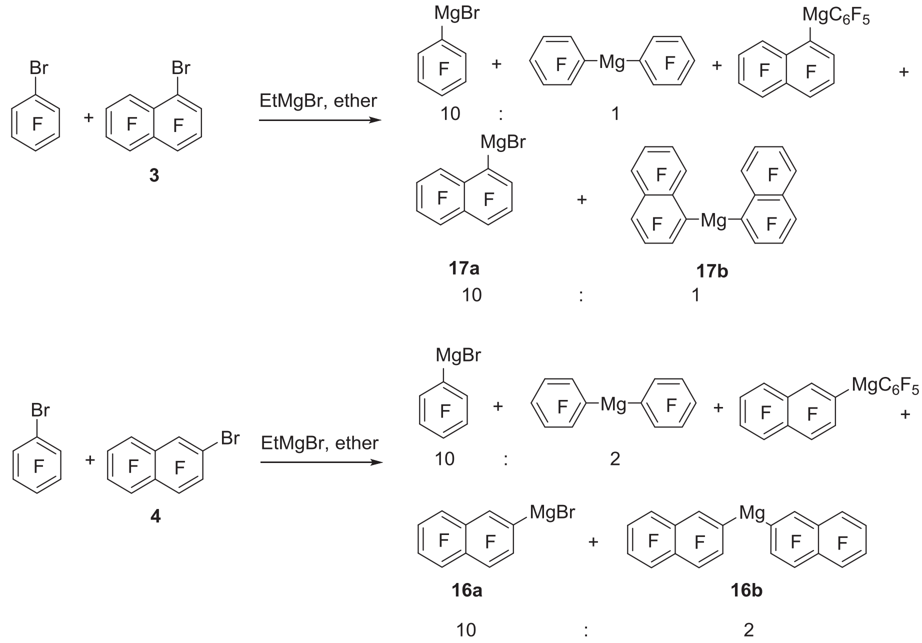
### 4.1. General

The NMR spectra were acquired using a Bruker Avance 300 ($^1H$ at 300.13 MHz, $^{19}F$ at 282.40 MHz) and an Avance 600 ($^{29}Si$ at 119.26 MHz) spectrometers. The chemical shifts were referenced to TMS ($^1H$, $^{29}Si$) and $CCl_3F$ ($^{19}F$, with $C_6F_6$ as secondary reference (−162.9 ppm)), respectively. The quantitative analysis of reaction mixtures was performed by the $^{19}F$ NMR spectroscopy with an internal standard $C_6H_5F$. GCMS analysis was performed using a Shimadzu GCMS-QP2010 Ultra (with GsBP-1MS column) instrument. High resolution mass spectra were recorded using a Thermo Scientific DFS spectrometer in EI mode (70 eV). Bromine was washed with concentrated $H_2SO_4$ and distilled. Chlorosulfonic acid was distilled. Ether was refluxed with sodium, distilled and stored over sodium pieces. Chlorotrimethylsilane was refluxed with $CaH_2$ and distilled. 1,2-Dibromoethane (DBE) was dried with $CaCl_2$ and distilled. Chloroheptafluoronaphthalenes were produced from $C_{10}Cl_8$ and KF and isolated by rectification [3]. 2-H-Heptafluoronaphthalene [15] and 2-bromoheptafluoronaphthalene [9] were prepared from 2-hydrazinoheptafluoronaphthalene by described procedures. Diisopropylamine (Acros), 2.5 M BuLi in hexanes (Acros), 1.6 M *t*-BuLi in pentanes (Acros) were used as supplied. Solution of EtMgBr was prepared from EtBr and magnesium and the concentration was determined by titration with acid.

All manipulations with organomagnesium and organolithium compounds were performed under an atmosphere of dry argon.

### 4.2. Preparation of heptafluoronaphthalenes

A three-necked flask (50 mL) equipped with a magnetic bar, dropping funnel and reflux condenser topped with T-adapter connected with argon line and bubbler was flushed with argon and charged with magnesium (255 mg, 10.4 mmol) and ether (15 mL). A



**Scheme 14.** Ratio of perfluoroarylmagnesiums in ether derived from a mixture of bromopentafluorobenzene and bromoheptafluoronaphthalene.

solution of chloroheptafluoronaphthalenes (40% of 1-$C_{10}F_7Cl$ and 60% of 2-$C_{10}F_7Cl$) (1.45 g, 5.0 mmol) and DBE (0.96 g, 5.1 mmol) in ether (10 mL) was added dropwise within 10 min to keep gentle reflux. The reaction mixture was refluxed with stirring for 4 h, cooled to the room temperature and poured onto ice acidified with HCl. The organic phase was separated, the aqueous phase extracted with ether (20 mL), the merged extract washed with brine and dried with $MgSO_4$. The solvent was removed on an evaporator to yield a mixture of chloroheptafluoronaphthalenes of 1-$C_{10}F_7Cl$ (6%), 2-$C_{10}F_7Cl$ (5%), 1-$C_{10}F_7H$ (32%) and 2-$C_{10}F_7H$ (56%) (1.2 g) ($^{19}$F NMR). Heptafluoronaphthalenes 1-$C_{10}F_7H$ (bp 122.9–124.1 °C at 60 Torr) and 2-$C_{10}F_7H$ (bp 130.5–131.1 °C at 60 Torr) were isolated by fractional vacuum-distilling a mixture collected from several experiments.

### *4.2.1. 1-H-heptafluoronaphthalene* ***1***

$^1$H NMR ($CDCl_3$): δ = 7.60 (dd, $^3J$(H$^1$, F$^2$) = 8.3 Hz, $^5J$(H$^1$, F$^4$) = 8.3 Hz, 1H, H$^1$). $^{19}$F NMR ($CDCl_3$): δ = −130.2 (ddddddd, $^3J$(F$^2$, H$^1$) = 9.5 Hz, $^3J$(F$^2$, F$^3$) = 20.0 Hz, $^4J$(F$^2$, F$^4$) = 8.2 Hz, $^7J$(F$^2$, F$^6$) = 8.2 Hz, $^6J$(F$^2$, F$^5$) = 5.9 Hz, $^5J$(F$^2$, F$^8$) = 3 Hz, $^6J$(F$^2$, F$^7$) = 2 Hz, 1F, F$^2$), −139.8 (ddddddd, $^4J$(F$^4$, H$^1$) = 9.5 Hz, $^4J$(F$^4$, F$^5$) = 52.6 Hz, $^3J$(F$^4$, F$^3$) = 16.1 Hz, $^4J$(F$^4$, F$^2$) = 8.5 Hz, $^5J$(F$^4$, F$^8$) = 4.4 Hz, $^5J$(F$^4$, F$^6$) = 4.4 Hz, $^6J$(F$^4$, F$^7$) = 2 Hz, 1F, F$^4$), −147.0 (dddddd, $^4J$(F$^5$, F$^4$) = 52.6 Hz, $^3J$(F$^5$, F$^6$) = 17.3 Hz, $^5J$(F$^5$, F$^8$) = 15.5 Hz, $^6J$(F$^5$, F$^2$) = 5.8 Hz, $^5J$(F$^5$, F$^3$) = 3.9 Hz, $^4J$(F$^5$, F$^7$) = 2 Hz, 1F, F$^5$), −148.2 (ddddd, $^3J$(F$^8$, F$^7$) = 17.8 Hz, $^5J$(F$^8$, F$^5$) = 15.8 Hz, $^5J$(F$^8$, F$^4$) = 5.7 Hz, $^6J$(F$^8$, F$^3$) = 3 Hz, $^5J$(F$^8$, F$^2$) = 2 Hz, 1F, F$^8$), −156.2 (ddddd, $^3J$(F$^7$, F$^8$) = 19.3 Hz, $^3J$(F$^7$, F$^6$) = 17.6 Hz, $^7J$(F$^7$, F$^3$) = 8.6 Hz, $^6J$(F$^7$, F$^4$) = 4.2 Hz, $^4J$(F$^7$, F$^5$) = 2 Hz, 1F, F$^7$), −157.0 (dddddd, $^3J$(F$^6$, F$^7$) = 19.2 Hz, $^3J$(F$^6$, F$^5$) = 17.1 Hz, $^7J$(F$^6$, F$^2$) = 8.3 Hz, $^5J$(F$^6$, F$^4$) = 4.9 Hz, $^6J$(F$^6$, F$^3$) = 2 Hz, $^4J$(F$^6$, F$^8$) = 2 Hz, 1F, F$^6$), −157.7 (dddddd, $^3J$(F$^3$, F$^2$) = 19.2 Hz, $^3J$(F$^3$, F$^4$) = 17.1 Hz, $^7J$(F$^3$, F$^7$) = 8.3 Hz, $^5J$(F$^3$, F$^5$) = 6.0 Hz, $^6J$(F$^3$, F$^6$) = 3 Hz, $^6J$(F$^3$, F$^8$) = 3 Hz, 1F, F$^3$).

### *4.2.2. 2-H-heptafluoronaphthalene* ***2***

$^1$H NMR ($CDCl_3$): δ = 7.17 (ddd, $^3J$(H$^2$, F$^1$) = 10.4 Hz, $^3J$(H$^2$, F$^3$) = 10.4 Hz, $^4J$(H$^2$, F$^4$) = 5.9 Hz, 1H, H$^2$). $^{19}$F NMR ($CDCl_3$): δ = −117.4 (dddddd, $^3J$(F$^1$, H$^2$) = 10.6 Hz, $^4J$(F$^1$, F$^8$) = 64.7 Hz, $^5J$(F$^1$, F$^4$) = 19.0 Hz, $^6J$(F$^1$, F$^6$) = 4.2 Hz, $^5J$(F$^1$, F$^7$) = 4.2 Hz, $^5J$(F$^1$, F$^5$) = 4.2 Hz, 1F, F$^1$), −134.8 (ddddddd, $^3J$(F$^3$, H$^2$) = 10.4 Hz, $^3J$(F$^3$, F$^4$) = 18.9 Hz, $^7J$(F$^3$, F$^7$) = 9.3 Hz, $^5J$(F$^3$, F$^5$) = 4.5 Hz, $^6J$(F$^3$, F$^6$) = 4.5 Hz, $^6J$(F$^3$, F$^8$) = 4.5 Hz, $^4J$(F$^3$, F$^1$) = 3 Hz, 1F, F$^3$), −145.3 (ddddd, $^4J$(F$^8$, F$^1$) = 64.7 Hz, $^3J$(F$^8$, F$^7$) = 17.4 Hz, $^5J$(F$^8$, F$^5$) = 16.2 Hz, $^5J$(F$^8$, F$^4$) = 4.2 Hz, $^4J$(F$^8$, F$^6$) = 3.7 Hz, 1F, F$^8$), −147.0 (ddddd, $^4J$(F$^5$, F$^4$) = 58.6 Hz, $^3J$(F$^5$, F$^6$) = 17.4 Hz, $^5J$(F$^5$, F$^8$) = 15.9 Hz, $^5J$(F$^5$, F$^1$) = 4.8 Hz, $^5J$(F$^5$, F$^3$) = 4.4 Hz, 1F, F$^5$), −150.5 (dddddd, $^4J$(F$^4$, F$^5$) = 58.6 Hz, $^3J$(F$^4$, F$^3$) = 18.7 Hz, $^5J$(F$^4$, F$^1$) = 17.8 Hz, $^4J$(F$^4$, H$^2$) = 5.6 Hz, $^5J$(F$^4$, F$^8$) = 4.8 Hz, $^6J$(F$^4$, F$^7$) = 4.8 Hz, 1F, F$^4$), −154.1 (m, 1F, F$^6$), −156.9 (ddddd, $^3J$(F$^7$, F$^6$) = 19.5 Hz, $^3J$(F$^7$, F$^8$) = 17.4 Hz, $^7J$(F$^7$, F$^3$) = 8.3 Hz, $^6J$(F$^7$, F$^4$) = 4.3 Hz, $^5J$(F$^7$, F$^1$) = 4.3 Hz, 1F, F$^7$).

## *4.3. Preparation of 1-bromoheptafluoronaphthalene* ***3***

### *4.3.1. 1-H-heptafluoronaphthalene (2.0 g, 7.87 mmol), iron filings (0.80 g, 14.3 mmol) and bromine (37.3 g, 12 mL, 233 mmol) were stirred at 22 °C for 2 h*

The solution was poured onto ice, residual bromine was neutralized with $Na_2S_2O_3$, the products were extracted with $CHCl_3$ (2 × 50 mL), the extract was washed with water and dried with $MgSO_4$. The solvent was distilled off on evaporator and the solid was sublimed (70–90°C at 0.1 Torr). The sublimate (1.76 g) consisted of 1-$C_{10}F_7Br$ (80%) and 1,5-$C_{10}Br_2F_6$ (20%) ($^{19}$F NMR).

### *4.3.2. 1-H-heptafluoronaphthalene (1.00 g, 3.93 mmol), bromine (0.76 g, 4.75 mmol) and chlorosulfonic acid (6 mL) were stirred at 22 °C for 2 h*

The solution was poured onto ice, the products were extracted with $CH_2Cl_2$ (2 × 10 mL), the extract was washed with 5% $Na_2SO_3$, with water and dried with $MgSO_4$. The solvent was distilled off on evaporator and the solid was dried in vacuum-desiccator over Sicapent® to yield 1-$C_{10}F_7Br$ (1.1 g, 84%).

*4.3.2.1. 1-Bromoheptafluoronaphthalene* ***3***. $^{19}$F NMR (ether): δ = −116.3 (dddddd, $^3J$(F$^2$, F$^3$) = 22.2 Hz, $^4J$(F$^2$, F$^4$) = 9.2 Hz, $^5J$(F$^2$, F$^8$) = 9.2 Hz, $^7J$(F$^2$, F$^6$) = 8.4 Hz, $^6J$(F$^2$, F$^5$) = 4.4 Hz, $^6J$(F$^2$, F$^7$) = 2.1 Hz 1F, F$^2$), −139.6 (ddddd, $^4J$(F$^4$, F$^5$) = 69.5 Hz, $^5J$(F$^4$, F$^8$) = 5.1 Hz, $^3J$(F$^4$,

$F^{3}) = 16.4$ Hz, $^{5}J(F^{4}, F^{6}) = 5.1$ Hz, $^{6}J(F^{4}, F^{7}) = 1.2$ Hz, 1F, $F^{4}$), −140.1 (ddddd, $^{3}J(F^{8}, F^{7}) = 16.3$ Hz, $^{5}J(F^{8}, F^{5}) = 15.9$ Hz, $^{5}J(F^{8}, F^{2}) = 9.3$ Hz, $^{6}J(F^{8}, F^{3}) = 3.4$ Hz, $^{5}J(F^{8}, F^{4}) = 5.3$ Hz, 1F, $F^{8}$), −145.0 (dddddd, $^{4}J(F^{5}, F^{4}) = 69.5$ Hz, $^{3}J(F^{5}, F^{6}) = 18.2$ Hz, $^{5}J(F^{5}, F^{8}) = 15.7$ Hz, $^{5}J(F^{5}, F^{3}) = 5.0$ Hz, $^{6}J(F^{5}, F^{2}) = 4.8$ Hz, $^{4}J(F^{5}, F^{7}) = 2.4$ Hz, 1F, $F^{5}$), −153.6 (ddddd, $^{3}J(F^{7}, F^{8}) = 17.0$ Hz, $^{3}J(F^{7}, F^{6}) = 19.3$ Hz, $^{7}J(F^{7}, F^{3}) = 9.0$ Hz, $^{6}J(F^{7}, F^{4})$ 4.5 Hz, $^{4}J(F^{7}, F^{5}) = 2.3$ Hz, 1F, $F^{7}$), −155.0 (dddddd, $^{3}J(F^{3}, F^{2}) = 22.2$ Hz, $^{3}J(F^{3}, F^{4}) = 17.0$ Hz, $^{7}J(F^{3}, F^{7}) = 8.6$ Hz, $^{5}J(F^{3}, F^{5}) = 5.3$ Hz, $^{6}J(F^{3}, F^{6}) = 5.3$ Hz, $^{6}J(F^{3}, F^{8}) = 3.0$ Hz, 1F, $F^{3}$), −155.2 (dddddd, $^{3}J(F^{6}, F^{7}) = 18.0$ Hz, $^{3}J(F^{6}, F^{5}) = 16.4$ Hz, $^{7}J(F^{6}, F^{2}) = 8.0$ Hz, $^{6}J(F^{6}, F^{3}) = 6.4$ Hz, $^{5}J(F^{6}, F^{4}) = 4.9$ Hz, $^{4}J(F^{6}, F^{8}) = 3.2$ Hz, 1F, $F^{6}$).

### *4.4. Attempted reaction of $C_6F_5H$ with EtMgBr*

The solution of $C_6F_5H$ (142 mg, 0.84 mmol) in ether (1 mL) was treated with 0.42 M EtMgBr (2 mL, 0.84 mmol) at 22 °C for 3 h. No reaction occurred ($^{19}$F NMR).

### *4.5. Attempted reaction of $C_{10}F_7H$ with EtMgBr*

The solution of **1** and **2** (1:4) (82 mg, 0.32 mmol) in ether (1 mL) was treated with 0.54 M EtMgBr (1 mL, 0.54 mmol) at 22 °C for 5 h. No reaction occurred ($^{19}$F NMR).

### *4.6. Reaction of 2-heptafluoronaphthyllithium with $ClSiMe_3$*

#### *4.6.1. A flame-dried flask equipped with a magnetic bar and septa was charged with **2** (254 mg, 1.00 mmol) and flushed with dry argon*

After the addition of ether (25 mL) the solution was cooled to −70 °C (bath) and stirred for 15 min. Then 2.5 M BuLi in hexanes (0.5 mL, 1.25 mmol) was injected slowly and the solution was stirred for 4 h before the injection of $ClSiMe_3$ (0.200 mL, 1.57 mmol). After 10 min it was warmed up to 20 °C within 20 min and hydrolyzed with 5% HCl (1 mL). The organic phase was separated, the aqueous phase extracted with ether (2 × 3 mL), the merged extract washed with brine and dried with $MgSO_4$. The $^{19}$F NMR spectrum of the extract showed the formation of **5** (0.80 mmol) that was obtained by removing of volatiles on evaporator.

#### *4.6.2. The reaction was performed by the same manner using 1.6 M t-BuLi in pentanes (1.12 mmol)*

The $^{19}$F NMR spectrum of the extract showed the formation of **5** (0.84 mmol). After the solvent evaporation silylnaphthalene **5** was isolated.

#### *4.6.3. A reactor (see above) was charged with ether (10 mL) and diisopropylamine (0.500 mL, 3.57 mmol)*

The solution was cooled to −60 °C (bath), stirred for 30 min, and 2.5 M BuLi in hexanes (1.4 mL, 3.5 mmol) was injected slowly and stirred for 30 min. In another flask a solution of **2** (254 mg, 1.00 mmol) in ether (22 mL) was cooled to −60 °C, and the solution of LDA (3.1 mL, 1.1 mmol) was syphoned into it at −60 °C under pressure of dry argon. The reaction mixture was stirred at this temperature for 4 h, treated with chlorotrimethylsilane (0.200 mL, 1.57 mmol), and the reaction mixture was worked up as described above. The $^{19}$F NMR spectrum of the extract showed the formation of **5** (0.94 mmol). After the solvent evaporation silylnaphthalene **5** was isolated.

#### *4.6.4. 2.5 M BuLi in hexanes (0.4 mL, 0.34 mmol) was dissolved in ether (2.5 mL) and injected into cold (−80 °C) solution of 2-$C_{10}F_7Br$ (100 mg, 0.30 mmol) in ether (6.5 mL)*

The reaction mixture was stirred for 1 h, a solution of chlorotrimethylsilane (0.39 mmol) in 0.25 mL of ether was added. After 20 min cooling bath was removed, the reaction mixture was allowed to warm to 20 °C within 1 h and worked up as described above to yield yellow oil (91 mg) contained 0.24 mmol (80%) of **5** ($^{19}$F NMR).

Analytically pure silylnaphthalene **5** was obtained by crystallization from ethanol.

*4.6.4.1. 2-Trimethylsilylheptafluoronaphthalene **5**.* $^{1}$H NMR (ether): δ = 0.45 (s, 9H). $^{19}$F NMR (ether): δ = −102.0 (dd, $^{4}J(F^{1}, F^{8}) = 73.8$ Hz, $^{5}J(F^{1}, F^{4}) = 20.1$ Hz, 1F, $F^{1}$), −124.3 (md, $^{3}J(F^{3}, F^{4}) = 19.2$ Hz, 1F, $F^{3}$), −144.2 (dddddd, $^{4}J(F^{8}, F^{1}) = 73.8$ Hz, $^{3}J(F^{8}, F^{7}) = 17.5$ Hz, $^{5}J(F^{8}, F^{5}) = 15.7$ Hz, $^{5}J(F^{8}, F^{4}) = 4.1$ Hz, $^{6}J(F^{8}, F^{3}) = 4.1$ Hz, $^{4}J(F^{8}, F^{6}) = 2$ Hz, 1F, $F^{8}$), −147.6 (dddddd, $^{4}J(F^{5}, F^{4}) = 57.0$ Hz, $^{3}J(F^{5}, F^{6}) = 17.3$ Hz, $^{5}J(F^{5}, F^{8}) = 15.7$ Hz, $^{5}J(F^{5}, F^{3}) = 4.6$ Hz, $^{5}J(F^{5}, F^{1}) = 2$ Hz, $^{4}J(F^{5}, F^{7}) = 2$ Hz, 1F, $F^{5}$), −151.3 (ddddd, $^{4}J(F^{4}, F^{5}) = 57.0$ Hz, $^{3}J(F^{4}, F^{3}) = 20.1$ Hz, $^{5}J(F^{4}, F^{1}) = 19.1$ Hz, $^{5}J(F^{4}, F^{6}) = 4.2$ Hz, $^{5}J(F^{4}, F^{8}) = 4.1$ Hz, 1F, $F^{4}$), −154.6 (m, 1F, $F^{6}$), −157.6 (ddddd, $^{3}J(F^{7}, F^{6}) = 18.9$ Hz, $^{3}J(F^{7}, F^{8}) = 17.3$ Hz, $^{7}J(F^{7}, F^{3}) = 7.5$ Hz, $^{5}J(F^{7}, F^{1}) = 4.1$ Hz, $^{4}J(F^{7}, F^{5}) = 1.3$ Hz, 1F, $F^{7}$). $^{1}$H NMR ($CCl_4$): δ = 0.45 (t, $^{5}J(H, F^{1,3}) = 1.5$ Hz, 9H). $^{19}$F NMR ($CCl_4$): δ = −103.3 (dd, $^{4}J(F^{1}, F^{8}) = 73.8$ Hz, $^{5}J(F^{1}, F^{4}) = 20.3$ Hz, 1F, $F^{1}$), −125.0 (md, $^{3}J(F^{3}, F^{4}) = 18.6$ Hz, 1F, $F^{3}$), −144.2 (ddddd, $^{4}J(F^{8}, F^{1}) = 73.8$ Hz, $^{3}J(F^{8}, F^{7}) = 16.8$ Hz, $^{5}J(F^{8}, F^{5}) = 16.8$ Hz, $^{5}J(F^{8}, F^{4}) = 3.3$ Hz, $^{6}J(F^{8}, F^{3}) = 3.3$ Hz, 1F, $F^{8}$), −147.6 (dddd, $^{4}J(F^{5}, F^{4}) = 57.0$ Hz, $^{3}J(F^{5}, F^{6}) = 16.8$ Hz, $^{5}J(F^{5}, F^{8}) = 16.8$ Hz, $^{5}J(F^{5}, F^{3}) = 4.5$ Hz, 1F, $F^{5}$), −151.3 (ddddd, $^{4}J(F^{4}, F^{5}) = 57.0$ Hz, $^{3}J(F^{4}, F^{3}) = 19.8$ Hz, $^{5}J(F^{4}, F^{1}) = 19.8$ Hz, $^{5}J(F^{4}, F^{6}) = 4.0$ Hz, $^{5}J(F^{4}, F^{8}) = 4.0$ Hz, 1F, $F^{4}$), −154.4 (m, 1F, $F^{6}$), −157.6 (dddd, $^{3}J(F^{7}, F^{6}) = 20.0$ Hz, $^{3}J(F^{7}, F^{8}) = 16.8$ Hz, $^{7}J(F^{7}, F^{3}) = 7.4$ Hz, $^{5}J(F^{7}, F^{1}) = 3.7$ Hz, 1F, $F^{7}$). $^{29}$Si{H} NMR ($CDCl_3$): δ = −0.92 (ddd, 4.5, 3.1 and 1.6 Hz). Found, %: C 48.0, H 2.78, F 40.6. $C_{13}H_9F_7Si$. Calc. %: C 47.85, H 2.78, F 40.76.

### *4.7. Reaction of 1-H-heptafluoronaphthalene with BuLi and $ClSiMe_3$*

The solution of **1** (254 mg, 1.00 mmol) in ether (25 mL) was cooled to −70 °C (bath) and stirred for 30 min. Then 2.5 M BuLi in hexanes (0.5 mL, 1.25. mmol) was injected slowly. After 4 h at −70 °C chlorotrimethylsilane (0.200 mL, 1.57 mmol) in ether (1 mL) was injected, the solution was stirred for 10 min and warmed up to 20 °C within 20 min. It was treated with 5% HCl (1 mL), the organic phase was separated, the aqueous phase extracted with ether (2 × 3 mL), the merged extract washed with brine (10 mL) and dried with $MgSO_4$. Evaporation of the volatiles gave yellow oil consisted of **1** (0.04 mmol), 1-H-3-$C_4H_9$–$C_{10}F_6$ (0.14 mmol), 1-H-6-$C_4H_9$–$C_{10}F_6$ (0.24 mmol), 1-H-7-$C_4H_9$–$C_{10}F_6$ (0.38 mmol), and 1-H-3,7-$(C_4H_9)_2C_{10}F_5$ (0.09 mmol) (GSMS and $^{19}$F NMR).

#### *4.7.1. 1-H-3-butylhexafluoronaphthalene **7***

$^{19}$F NMR (acetone): δ{δ*}[1] = −112.3 {−113.3} (m, 1F, $F^{2}$), −117.3 {−116.5} (dd, $^{4}J(F^{4}, F^{5}) = 61$ Hz, $^{4}J(F^{4}, F^{2}) = 8$ Hz, 1F, $F^{4}$), −146.3 {−147.2} (ddd, $^{4}J(F^{5}, F^{4}) = 61$ Hz, $^{3}J(F^{5}, F^{6}) = 16$ Hz, $^{5}J(F^{5}, F^{8}) = 16$ Hz, 1F, $F^{5}$), −148.9 {−149.9} (dd, $^{5}J(F^{8}, F^{5}) = 16$ Hz, $^{3}J(F^{8}, F^{7}) = 16$ Hz, 1F, $F^{8}$), −157.5 {−157.5} (dd, $^{3}J(F^{7}, F^{6}) = 18$ Hz, $^{3}J(F^{7}, F^{8}) = 16$ Hz, 1F, $F^{7}$), −159.8 {−159.7} (dddd, $^{3}J(F^{6}, F^{7}) = 18$ Hz, $^{3}J(F^{6}, F^{5}) = 16$ Hz, $^{7}J(F^{6}, F^{2}) = 7$ Hz, $^{4}J(F^{6}, F^{8}) = 4$ Hz, 1F, $F^{6}$).

#### *4.7.2. 1-H-6-butylhexafluoronaphthalene **8***

$^{19}$F NMR (acetone): δ{δ*}[1] = −123.8 {−123.7} (dd, $^{4}J(F^{5}, F^{4}) = 61$ Hz, $^{5}J(F^{5}, F^{8}) = 19$ Hz, 1F, $F^{5}$), −131.1 {−131.5} (m, 1F, $F^{2}$), −139.5 {−140.0} (dd, $^{4}J(F^{4}, F^{5}) = 61$ Hz, $^{3}J(F^{3}, F^{4}) = 17$ Hz, 1F, $F^{4}$), −140.5 {−139.3} (d, $^{3}J(F^{7}, F^{8}) = 18$ Hz, 1F, $F^{7}$), −151.7 {−153.4}

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[1] δ* is chemical shift calculated according to the incremental scheme.

(dd, $^3J$(F$^8$, F$^7$) = 18 Hz, $^5J$(F$^8$, F$^5$) = 19 Hz, 1F, F$^8$), −160.2 {−160.4} (m, 1F, F$^3$).

#### 4.7.3. 1-H-7-butylhexafluoronaphthalene **9**

$^{19}$F NMR (acetone): δ{δ*}$^1$ = −126.5 {−124.9} (d, $^3J$(F$^8$, F$^7$) = 18 Hz, 1F, F$^8$), −132.6 {−132.9} (m, 1F, F$^2$), −141.3 {−141.5} (m, 1F, F$^4$), −141.3 {−140.1} (m, 1F, F$^6$), −151.0 {−152.2} (ddd, $^4J$(F$^5$, F$^4$) = 50 Hz, $^3J$(F$^5$, F$^6$) = 18 Hz, $^5J$(F$^5$, F$^8$) = 18 Hz, 1F, F$^5$), −158.9 {−159.0} (dd, $^3J$(F$^3$, F$^2$) = 18 Hz, $^3J$(F$^3$, F$^4$) = 18 Hz, 1F, F$^3$).

#### 4.7.4. 1-H-3,7-dibutylpentafluoronaphthalene **10**

$^{19}$F NMR (acetone): δ{δ*}$^1$ = −114.6 {−116.0} (m, 1F, F$^2$), −118.4 {−117.2} (dd, $^4J$(F$^4$, F$^5$) = 58 Hz, $^4J$(F$^4$, F$^2$) = 7 Hz, 1F, F$^4$), −128.2 {−126.3} (d, $^5J$(F$^8$, F$^5$) = 18 Hz, 1F, F$^8$), −143.8 {−142.8} (m, $^3J$(F$^6$, F$^5$) = 17 Hz, 1F, F$^6$), −150.2 {−152.4} (ddd, $^4J$(F$^5$, F$^4$) = 58 Hz, $^3J$(F$^5$, F$^6$) = 17 Hz, $^5J$(F$^5$, F$^8$) = 18 Hz, 1F, F$^5$).

### 4.8. Reaction of 1-H-heptafluoronaphthalene with t-BuLi and ClSiMe$_3$

The reaction was performed by the same manner using 1.6 M *t*-BuLi in pentanes (1.12 mmol). Evaporation of volatiles gave yellow oil consisted of **1** (0.14 mmol), 1-H-3-*t*-$C_4H_9$−$C_{10}F_6$ **11** (0.07 mmol), 1-H-6-*t*-$C_4H_9$−$C_{10}F_6$ **12** (0.13 mmol), 1-H-7-*t*-$C_4H_9$−$C_{10}F_6$ **13** (0.16 mmol), 1-H-2,6-(*t*-$C_4H_9$)$_2C_{10}F_5$ **14** (0.10 mmol), and 1-H-3,7-(*t*-$C_4H_9$)$_2C_{10}F_5$ **15** (0.23 mmol) (GSMS, $^{19}$F NMR).

#### 4.8.1. 1-H-3-t-butylhexafluoronaphthalene **11**

$^{19}$F NMR (acetone): δ{δ*}$^1$ = −102.0 {−106.5} (m, 1F, F$^2$), −108.5 {−108.0} (d, $^4J$(F$^4$, F$^5$) = 75 Hz, 1F, F$^4$), −144.9 {−144.9} (ddd, $^4J$(F$^5$, F$^4$) = 75 Hz, $^3J$(F$^5$, F$^6$) = 17 Hz, $^5J$(F$^5$, F$^8$) = 17 Hz, 1F, F$^5$), −149.7 {−149.8} (ddd, $^5J$(F$^8$, F$^5$) = 17 Hz, $^3J$(F$^8$, F$^7$) = 16 Hz, $^4J$(F$^8$, F$^6$) = 4 Hz, 1F, F$^8$), −157.0 {−156.7} (dd, $^3J$(F$^7$, F$^6$) = 19 Hz, $^3J$(F$^7$, F$^8$) = 16 Hz, 1F, F$^7$), −159.6 {−159.2} (dddd, $^3J$(F$^6$, F$^7$) = 19 Hz, $^3J$(F$^6$, F$^5$) = 17 Hz, $^7J$(F$^6$, F$^2$) = 8 Hz, $^4J$(F$^6$, F$^8$) = 4 Hz, 1F, F$^6$).

#### 4.8.2. 1-H-6-t-butylhexafluoronaphthalene **12**

$^{19}$F NMR (acetone): δ{δ*}$^1$ = −115.5 {−115.2} (dd, $^4J$(F$^5$, F$^4$) = 75 Hz, $^5J$(F$^5$, F$^8$) = 15 Hz, 1F, F$^5$), −130.6 {−130.7} (m, 1F, F$^2$), −132.7 {−132.5} (m, 1F, F$^7$), −138.2 {−137.7} (d, $^4J$(F$^4$, F$^5$) = 75 Hz, 1F, F$^4$), −151.0 {−151.7} (dd, $^3J$(F$^8$, F$^7$) = 18 Hz, $^5J$(F$^8$, F$^5$) = 15 Hz, 1F, F$^8$), −159.9 {−159.9} (ddddd, $^3J$(F$^3$, F$^2$) = 19 Hz, $^3J$(F$^3$, F$^4$) = 16 Hz, $^7J$(F$^3$, F$^7$) = 8 Hz, $^5J$(F$^3$, F$^5$) = 73 Hz, $^6J$(F$^3$, F$^8$) = 4 Hz, 1F, F$^3$).

#### 4.8.3. 1-H-7-t-butylhexafluoronaphthalene **13**

$^{19}$F NMR (acetone): δ{δ*}$^1$ = −118.1 {−116.4} (d, $^5J$(F$^8$, F$^5$) = 16 Hz, 1F, F$^8$), −132.8 {−132.4} (m, 1F, F$^2$), −133.7 {−133.3} (m, 1F, F$^6$), −141.8 {−141.4} (dd, $^4J$(F$^4$, F$^5$) = 47 Hz, $^3J$(F$^4$, F$^3$) = 16 Hz, 1F, F$^4$), −150.4 {−150.5} (ddd, $^4J$(F$^5$, F$^4$) = 47 Hz, $^3J$(F$^5$, F$^6$) = 17 Hz, $^5J$(F$^5$, F$^8$) = 16 Hz, 1F, F$^5$), −158.5 {−158.2} (dd, $^3J$(F$^3$, F$^2$) = 19 Hz, $^3J$(F$^3$, F$^4$) = 16 Hz, 1F, F$^3$).

#### 4.8.4. 1-H-2,6-di(t-butyl)pentafluoronaphthalene **14**

$^{19}$F NMR (acetone): δ{δ*}$^1$ = −116.7 {−116.8} (dd, $^4J$(F$^5$, F$^4$) = 71 Hz, $^5J$(F$^5$, F$^8$) = 15 Hz, 1F, F$^5$), −136.0 {−136.2} (m, 1F, F$^3$) (overlaps with F$^6$ of **15**), −144.0 {−141.2} (dd, $^4J$(F$^4$, F$^5$) = 71 Hz, $^3J$(F$^4$, F$^3$) = 13 Hz, 1F, F$^4$), −135.4 {−134.7} (d, $^3J$(F$^7$, F$^8$) = 14 Hz, 1F, F$^7$), −152.7 {−149.6} (dd, $^3J$(F$^7$, F$^8$) = 17 Hz, $^5J$(F$^5$, F$^8$) = 15 Hz, 1F, F$^8$).

#### 4.8.5. 1-H-3,7-di(t-butyl)pentafluoronaphthalene **15**

$^{19}$F NMR (acetone): δ{δ*}$^1$ = −104.6 {−108.7} (m, 1F, F$^2$), −110.2 {−109.6} (d, $^4J$(F$^4$, F$^5$) = 70 Hz, 1F, F$^4$), −120.7 {−118.0} (d, $^4J$(F$^8$, F$^6$) = 17 Hz, 1F, F$^8$), −136.0 {−135.5} (m, 1F, F$^6$) (overlaps with F$^3$ of **14**), −148.6 {−148.4} (ddd, $^4J$(F$^5$, F$^4$) = 70 Hz, $^3J$(F$^5$, F$^6$) = 15 Hz, $^5J$(F$^5$, F$^8$) = 15 Hz, 1F, F$^5$).

### 4.9. Attempted reaction of 1-H-heptafluoronaphthalene with LDA and ClSiMe$_3$

The solution of **1** (254 mg, 1.00 mmol) in ether (21 mL) was cooled to −60 °C and solution of LDA (3.1 mL, 1.1 mmol) (from 0.500 mL (3.57 mmol) of *i*-Pr$_2$NH and 1.3 mL (3.25 mmol) of 2.5 M BuLi in 8 mL of ether)) was injected slowly to keep temperature −(65 to 55) °C. The reaction mixture was stirred at this temperature for 4 h. Chlorotrimethylsilane (0.200 mL, 1.57 mmol) was injected and then the reaction mixture was worked up as described above. The $^{19}$F NMR spectrum of the extract showed signals of only **1** (0.80 mmol).

### 4.10. Reaction of 1-H-heptafluoronaphthalene with BuLi

A flame-dried flask equipped with a magnetic bar and septa was charged with **1** (127 mg, 0.50 mmol) and ether (11.5 mL). The solution was cooled to −80 °C (bath) and stirred for 15 min. 2.5 M BuLi in hexanes (0.4 mL) was dissolved in ether (1.6 mL), and 1 mL of this solution (0.50 mmol) was injected slowly into the reactor. The solution was stirred for 15 min and the saturated aqueous solution of water in ether (prepared from 5% HCl and ether, 1:4, v/v) was injected. The reaction mixture was allowed to warm to 22 °C, treated with K$_2$CO$_3$ and washed with brine (10 mL). The organic phase was separated, the aqueous phase extracted with ether (2 × 3 mL) and the merged extract dried with MgSO$_4$. The solvent was evaporated at reduced pressure and the residue was dissolved in acetone. The product consisted of **1** (0.32 mmol), **7** (0.04 mmol), **8** (0.05 mmol) and **9** (0.08 mmol) (GCMS, $^{19}$F NMR).

### 4.11. Reaction of 1-bromoheptafluoronaphthalene with BuLi

A flame-dried flask equipped with a magnetic bar and septa was charged with **3** (103 mg, 0.30 mmol) and ether (6.5 mL). The solution was cooled to −80 °C (bath) and stirred for 15 min. 2.5 M BuLi in hexanes (0.3 mL) was dissolved in ether (2.5 mL) and 1 mL of the solution (0.27 mmol) was injected slowly into the reactor. The solution was stirred for 15 min and saturated aqueous solution of water in ether (prepared from 5% HCl and ether, 1:4, v/v) was injected. The reaction mixture was allowed to warm to 22 °C treated as above. The product consisted of **1** (0.18 mmol) and **3** (0.07 mmol) ($^{19}$F NMR).

### 4.12. Reaction of 1-bromoheptafluoronaphthalene with BuLi and ClSiMe$_3$

2.5 M BuLi in hexanes (0.4 mL, 1.25 mmol) was diluted with ether (2.8 mL) and injected slowly into cold (−80 °C, bath) solution of **3** (102 mg, 0.30 mmol) in ether (6.5 mL). After 1 h at −80 °C chlorotrimethylsilane (0.10 mL, 2.57 mmol) was injected, solution was stirred 15–20 min and a saturated aqueous solution of water in ether (1 mL) (prepared from 5% HCl and ether, 1:4, v/v) was injected. The reaction mixture was allowed to warm to 22 °C, washed with brine (8 mL) and K$_2$CO$_3$, the organic phase was separated, the aqueous phase extracted with ether (2 × 4 mL), the merged extract was dried with MgSO$_4$. Evaporation of volatiles gave yellow oil (80 mg) consisted of **1** (0.81 mmol), and **6** (142 mmol) (GSMS and $^{19}$F NMR).

### 4.13. Reaction of 2-bromoheptafluoronaphthalene with magnesium

A flask equipped with a magnetic bar, septum and a reflux condenser topped with T-adapter connected with argon line and bubbler with conc. $H_2SO_4$ was flushed with argon and charged with magnesium turnings (63 mg, 2.6 mmol) and ether (6 mL). The solution of DBE (91 mg, 0.48 mmol) in ether (2 mL) was added and, after 5–7 min, the solution of **4** (513 mg, 1.54 mmol) in ether (4 mL) was injected within 10 min. The reaction mixture was refluxed with stirring for 2 h, and cooled to the room temperature. A probe of the mother liquid over magnesium was taken under dry argon atmosphere. The $^{19}$F NMR spectrum showed signals of 2-$C_{10}F_7MgBr$ (0.42 mmol), (2-$C_{10}F_7)_2Mg$ (0.21 mmol), **4** (0.09 mmol) and **2** (0.40 mmol). In next 4 h of refluxing, **4** disappeared and amounts of **16a**, **16b** and **2** were 0.52, 0.18 and 0.49 mmol, respectively.

In a similar manner, a reaction of **4** (656 mg, 1.97 mmol) with magnesium powder (83 mg, 3.41 mmol), and DBE (126 mg, 0.67 mmol) in ether (13 mL) gave 2-$C_{10}F_7MgBr$ (0.73 mmol), (2-$C_{10}F_7)_2Mg$ (0.36 mmol), **4** (0.10 mmol) and **2** (0.68 mmol) after 2 h of refluxing

### *4.14. Reaction of 2-bromoheptafluoronaphthalene with ethylmagnesium bromide*

A reactor (see above) was charged with **4** (274 mg, 0.82 mmol) in ether (1 mL), and 0.42 M EtMgBr in ether (2.0 mL, 0.84 mmol) was injected slowly under cooling of the reactor with cold water. The solution was stirred at 22 °C for 2 h. The $^{19}$F NMR spectrum showed signals of 2-$C_{10}F_7MgBr$ (0.60 mmol), (2-$C_{10}F_7)_2Mg$ (0.12 mmol) and trace of **2**. After dilution in half the ratio **16a**:**16b** was not changed.

#### *4.14.1. 2-Heptafluoronaphthylmagnesium bromide* ***16a***

$^{19}$F NMR (ether): δ = −90.37 (dd, $^{4}J$(F$^{1}$, F$^{8}$) = 68 Hz, $^{5}J$(F$^{1}$, F$^{4}$) = 24 Hz, 1F, F$^{1}$), −108.10 (d, $^{3}J$(F$^{3}$, F$^{4}$) = 28 Hz, 1F, F$^{3}$), −145.68 (ddd, $^{4}J$(F$^{8}$, F$^{1}$) = 68 Hz, $^{3}J$(F$^{8}$, F$^{7}$) = 17 Hz, $^{5}J$(F$^{8}$, F$^{5}$) = 17 Hz, 1F, F$^{8}$), −149.10 (ddd, $^{4}J$(F$^{5}$, F$^{4}$) = 56 Hz, $^{3}J$(F$^{5}$, F$^{6}$) = 14 Hz, $^{5}J$(F$^{5}$, F$^{8}$) = 17 Hz, 1F, F$^{5}$), −153.33 (ddd, $^{4}J$(F$^{4}$, F$^{5}$) = 56 Hz, $^{5}J$(F$^{4}$, F$^{1}$) = 24 Hz, $^{3}J$(F$^{4}$, F$^{3}$) = 28 Hz, 1F, F$^{4}$), −159.94 (dd, $^{3}J$(F$^{6}$, F$^{7}$) = 18 Hz, $^{3}J$(F$^{6}$, F$^{5}$) = 14 Hz, 1F, F$^{6}$), −161.55 (dd, $^{3}J$(F$^{7}$, F$^{8}$) = 18 Hz, $^{3}J$(F$^{7}$, F$^{6}$) = 18 Hz, 1F, F$^{7}$).

#### *4.14.2. Bis(2-heptafluoronaphthyl)magnesium* ***16b***

$^{19}$F NMR (ether): δ = −90.73 (dd, $^{4}J$(F$^{1}$, F$^{8}$) = 68 Hz, $^{5}J$(F$^{1}$, F$^{4}$) = 25 Hz, 2F, F$^{1}$), −108.32 (d, $^{3}J$(F$^{3}$, F$^{4}$) = 28 Hz, 2F, F$^{3}$), −146.49 (dddd, $^{4}J$(F$^{8}$, F$^{1}$) = 68 Hz, $^{3}J$(F$^{8}$, F$^{7}$) = 16 Hz, $^{5}J$(F$^{8}$, F$^{5}$) = 16 Hz, $^{4}J$(F$^{8}$, F$^{6}$) = 5 Hz, 2F, F$^{8}$), −149.14 (ddd, $^{4}J$(F$^{5}$, F$^{4}$) = 59 Hz, $^{3}J$(F$^{5}$, F$^{6}$) = 14 Hz, $^{5}J$(F$^{5}$, F$^{8}$) = 16 Hz, 2F, F$^{5}$), −153.43 (ddd, $^{4}J$(F$^{4}$, F$^{5}$) = 56 Hz, $^{5}J$(F$^{4}$, F$^{1}$) = 24 Hz, $^{3}J$(F$^{4}$, F$^{3}$) = 28 Hz, 2F, F$^{4}$), −160.12 (dd, $^{3}J$(F$^{6}$, F$^{7}$) = 18 Hz, $^{3}J$(F$^{6}$, F$^{5}$) = 14 Hz, 2F, F$^{6}$), −161.62 (dd, $^{3}J$(F$^{7}$, F$^{8}$) = 16 Hz, $^{3}J$(F$^{7}$, F$^{6}$) = 18 Hz, 2F, F$^{7}$).

### *4.15. Reaction of 2-heptafluoronaphthylmagnesium derivatives, 2-$C_{10}F_7MgX$, with $ClSiMe_3$*

#### *4.15.1. The solution of 2-$C_{10}F_7MgX$ (X = Br and 2-$C_{10}F_7$) (from* ***4*** *(347 mg, 1.0 mmol), ether (5 mL) and 0.42 M EtMgBr in ether (4.8 mL, 2.0 mmol)) was stirred at 22 °C for 1 h and $ClSiMe_3$ (0.30 mL, 2.36 mmol) in THF (2.5 mL) was injected under cooling with cold water within 1 min*

Formed white suspension was stirred for 2 h and hydrolyzed with 5% HCl (5 mL). The organic phase was separated, the aqueous phase extracted with ether (5 mL), the merged extract washed with brine and dried with $MgSO_4$. The solvent was evaporated, and brown oil was passed through a column with alumina (eluent petroleum ether (40–60 °C)). The solvent was removed on the evaporator to yield **5** (colorless oil) (255 mg, 78%).

#### *4.15.2. The Grignard reagent (from* ***4*** *(513 mg, 1.54 mmol), magnesium (63 mg, 2.6 mmol), DBE (91 mg, 0.48 mmol) in ether (16 mL)) were refluxed for 6 h, and $ClSiMe_3$ (127 mg, 1.17 mmol) in ether (3 mL) was added*

The reaction mixture was refluxed for 2 h. The $^{19}$F NMR spectrum showed resonances of **2** (0.49 mmol), **16a** (0.52 mmol), and **16b** (0.17 mmol). The further refluxing for 5 h gave a mixture of **2** (1.30 mmol), **16a** and **16b** (0.07 mmol) and **5** (0.24 mmol).

### *4.16. Formation of $C_6F_5MgX$ (X = Br, $C_6F_5$) and its reaction with $ClSiMe_3$*

A bottle (5 mL) equipped with a magnetic bar was sealed with AluCap®, flushed with argon and charged with $C_6F_5Br$ (208 mg, 0.84 mmol) in ether (1 mL). Then a solution of 0.42 M EtMgBr in ether (2.0 mL, 0.84 mmol) was injected in portions under cooling of the reactor with cold water. The solution was stirred at 22 °C for 2 h. The $^{19}$F NMR spectrum showed signals of $C_6F_5MgBr$ (0.57 mmol) and $(C_6F_5)_2Mg$ (0.14 mmol). The reaction mixture was treated with $ClSiMe_3$ (0.2 mL) and stirred at 22 °C for 4 h. The $^{19}$F NMR spectrum showed signals of $C_6F_5MgBr$, $(C_6F_5)_2Mg$, $C_6F_5SiMe_3$ and $C_6F_5H$ (10:4:1:3). In 50 h, resonances of $C_6F_5MgX$ disappeared and $C_6F_5SiMe_3$ and $C_6F_5H$ were present (10:8).

### *4.17. Reaction of 1-bromoheptafluoronaphthalene with magnesium*

#### *4.17.1. The solution of* ***3*** *(167 mg, 0.50 mmol) and DBE (37 mg, 0.20 mmol) in ether (1.5 mL) was added to magnesium (19 mg, 0.76 mmol) in ether (1.5 mL)*

The stirred solution was kept at 36–40 °C and hydrolyzed to give **3** (0.36 mmol) and **1** (0.16 mmol) ($^{19}$F NMR).

#### *4.17.2. A reactor (see above) was charged with magnesium (27 mg, 1.1 mmol) and ether (1.8 mL)*

The solution of **3** (110 mg, 0.33 mmol), DBE (92 mg, 0.49 mmol) in ether (1.3 mL) was injected in portions and the reaction mixture was refluxed with stirring for 3 h. A probe of the mother liquid over magnesium was taken at dry argon atmosphere. The $^{19}$F NMR spectrum showed signals of (1-$C_{10}F_7)_2Mg$ (0.10 mmol), **3** (0.04 mmol) and **1** (0.15 mmol). In next 2 h of refluxing **17b** (0.11 mmol), **3** (0.04 mmol) and **1** (0.18 mmol) were found.

### *4.18. Reaction of 1-bromoheptafluoronaphthalene with ethylmagnesium bromide*

#### *4.18.1. A flask equipped with a magnetic bar and septa was charged with 0.54 M EtMgBr in ether (1.0 mL, 0.54 mmol) cooled with ice water, and the solution of* ***3*** *(108 mg, 0.32 mmol) in ether (1 mL) was added with syringe*

The solution was kept at 20 °C for 2 h. The $^{19}$F NMR spectrum showed signals of 1-$C_{10}F_7MgBr$ and (1-$C_{10}F_7)_2Mg$ (10:1).

#### *4.18.2. A flask equipped with a magnetic bar and septa was charged with the solution of* ***3*** *(111 mg, 0.33 mmol) in ether (1 mL), cooled with ice water, and 0.54 M EtMgBr in ether (0.50 mL, 0.27 mmol) was added with a syringe*

The solution was stirred at 20 °C for 2 h. The $^{19}$F NMR spectrum showed signals of 1-$C_{10}F_7MgBr$ (0.20 mmol), (1-$C_{10}F_7)_2Mg$ (0.04 mmol) and residual **3** (0.07 mmol).

*4.18.2.1. 1-Heptafluoronaphthylmagnesium bromide* ***17a****.* $^{19}$F NMR (ether): δ = −106.8 (br, $\omega_{1/2}$ = 98 Hz, 1F, F$^{2}$), −143.0 (br, $\omega_{1/2}$ = 109 Hz, 1F, F$^{8}$), −145.9 (d, $^{4}J$(F$^{4}$, F$^{5}$) = 52 Hz, 1F, F$^{4}$), −148.1 (d, $^{4}J$(F$^{5}$, F$^{4}$) = 52 Hz, 1F, F$^{5}$), −159.2 (dddd, $^{3}J$(F$^{3}$, F$^{2}$) = 35 Hz, $^{3}J$(F$^{3}$, F$^{4}$) = 15 Hz, $^{5}J$(F$^{3}$, F$^{5}$) = 7 Hz, $^{7}J$(F$^{3}$, F$^{7}$) = 8 Hz, 1F, F$^{3}$), −161.4 (dd, $^{3}J$(F,

F) = 20 Hz, $^{3}J$(F, F) = 20 Hz, 1F) and −161.6 (dd, $^{3}J$(F, F) = 20 Hz, $^{3}J$(F, F) = 20 Hz, 1F) (F$^{6}$ and F$^{7}$).

### *4.18.2.2. Bis(1-heptafluoronaphthyl)magnesium* ***17b***.

$^{19}$F NMR (ether): δ = −106.90 (d, $^{3}J$(F$^{2}$, F$^{3}$) = 37 Hz, 2F, F$^{2}$), −142.2 (dd, $^{3}J$(F$^{8}$, F$^{7}$) = 15 Hz, $^{5}J$(F$^{8}$, F$^{5}$) = 15 Hz, 2F, F$^{8}$), −146.1 (d, $^{4}J$(F$^{4}$, F$^{5}$) = 52 Hz, 2F, F$^{4}$), −148.3 (dddd, $^{4}J$(F$^{5}$, F$^{4}$) = 52 Hz, $^{3}J$(F$^{5}$, F$^{6}$) = 15 Hz, $^{5}J$(F$^{5}$, F$^{8}$) = 15 Hz, $^{4}J$(F$^{5}$, F$^{7}$) = 6 Hz, 2F, F$^{5}$), −159.3 (dddd, $^{3}J$(F$^{3}$, F$^{2}$) = 35 Hz, $^{3}J$(F$^{3}$, F$^{4}$) = 14 Hz, $^{7}J$(F$^{3}$, F$^{7}$) = 7 Hz, $^{6}J$(F$^{3}$, F$^{6}$) = 7 Hz, 2F, F$^{3}$), −161.5 (dd, $^{3}J$(F$^{6}$, F$^{5}$) = 19 Hz, $^{3}J$(F$^{6}$, F$^{7}$) = 19 Hz, 2F, F$^{6}$), −161.6 (dd, $^{3}J$(F$^{7}$, F$^{8}$) = 19 Hz, $^{3}J$(F$^{7}$, F$^{6}$) = 19 Hz, 2F, F$^{7}$).

### *4.19. Reaction of 1-heptafluoronaphthylmagnesium derivatives, 1-$C_{10}F_7MgX$, with $ClSiMe_3$*

The solution of 1-$C_{10}F_7MgX$ (X = Br and 1-$C_{10}F_7$) (from **3** (105 mg, 0.31 mmol), ether (1 mL) and 0.54 M EtMgBr in ether (1 mL, 0.54 mmol)) was stirred at 22 °C for 1 h and the flask was cooled with ice water. Chlorotrimethylsilane (0.06 mL, 0.5 mmol) in THF (1 mL) was injected within 1 min. The formed white suspension was stirred for 2 h. After hydrolysis with 5% HCl (5 mL) the organic phase was separated, the aqueous phase extracted with ether (5 mL) and the merged extract dried with $MgSO_4$. Evaporation of volatiles gave **6** and **1** (4:1) (83 mg).

### *4.19.1. 1-Trimethylsilylheptafluoronaphthalene* ***6***

$^{1}$H NMR ($CCl_4$): δ = 0.45 (d 3.3 Hz, d 4.7 Hz, 9H). $^{19}$F NMR ($CCl_4$): δ = −111.8 (m, 1F, F$^{2}$), −133.9 (m, 1F, F$^{8}$), −138.6 (ddd, $^{4}J$(F$^{4}$, F$^{5}$) = 66 Hz, $^{3}J$(F$^{4}$, F$^{3}$) = 15 Hz, $^{5}J$(F$^{4}$, F$^{8}$) = 15 Hz, 1F, F$^{4}$), −146.1 (ddddd, $^{4}J$(F$^{5}$, F$^{4}$) = 66 Hz, $^{3}J$(F$^{5}$, F$^{6}$) = 19.6 Hz, $^{5}J$(F$^{5}$, F$^{8}$) = 12.5 Hz, $^{5}J$(F$^{5}$, F$^{3}$) = 5.6 Hz, $^{4}J$(F$^{5}$, F$^{7}$) = 3 Hz, 1F, F$^{5}$), −156.7 (ddd, $^{3}J$(F$^{7}$, F$^{6}$) = 19.4 Hz, $^{3}J$(F$^{7}$, F$^{8}$) = 19.4 Hz, $^{7}J$(F$^{7}$, F$^{3}$) = 8.4 Hz, 1F, F$^{7}$), −157.6 (tm 19 Hz) and −157.8 (tm 19 Hz) (2F, F$^{3}$ and F$^{6}$). $^{19}$F NMR (ether + THF): δ = −110.9 (m, 1F, F$^{2}$), −132.0 (m, 1F, F$^{8}$), −138.3 (ddddd, $^{4}J$(F$^{4}$, F$^{5}$) = 66 Hz, $^{3}J$(F$^{4}$, F$^{3}$) = 16.5 Hz, $^{5}J$(F$^{4}$, F$^{8}$) = 12.8 Hz, $^{5}J$(F$^{4}$, F$^{6}$) = 4 Hz, $^{4}J$(F$^{4}$, F$^{2}$) = 4 Hz, 1F, F$^{4}$), −146.1 (ddddd, $^{4}J$(F$^{5}$, F$^{4}$) = 66 Hz, $^{3}J$(F$^{5}$, F$^{6}$) = 18.3 Hz, $^{5}J$(F$^{5}$, F$^{8}$) = 13.7 Hz, $^{5}J$(F$^{5}$, F$^{3}$) = 5.9 Hz, $^{4}J$(F$^{5}$, F$^{7}$) = 4 Hz, 1F, F$^{5}$), −156.5 (dddd, $^{3}J$(F$^{7}$, F$^{6}$) = 19.9 Hz, $^{3}J$(F$^{7}$, F$^{8}$) = 18.1 Hz, $^{7}J$(F$^{7}$, F$^{3}$) = 8.6 Hz, $^{4}J$(F$^{7}$, F$^{5}$) = 4 Hz, 1F, F$^{7}$), −157.6 (tm, 20 Hz) and −157.7 (tm, 20 Hz) (2F, F$^{3}$ and F$^{6}$). $^{29}$Si {H} NMR ($CCl_4$): δ = −0.08 (d, 3 Hz, d, 7 Hz). Found: M/z$^{+}$ 326.0370. $C_{13}H_9F_7Si$. Calc.: 326.0361.

### *4.20. Reaction of 1-$C_{10}F_7Br$ and $C_6F_5Br$ with ethylmagnesium bromide*

A flame-dried flask equipped with a magnetic bar and septa was flushed with argon and charged with 1-$C_{10}F_7Br$ (104 mg, 0.31 mmol) and $C_6F_5Br$ (82 mg, 0.33 mmol) in ether (3 mL). Then 0.42 M EtMgBr in ether (2.7 mL, 1.1 mmol) was injected under cooling of the flask with cold water. The solution was stirred at 22 °C for 2 h. The $^{19}$F NMR spectrum showed signals of 1-$C_{10}F_7MgBr$, (1-$C_{10}F_7)_2Mg$, $C_6F_5MgBr$, $(C_6F_5)_2Mg$ and, probably, 1-$C_{10}F_7MgC_6F_5$ in 10:1:10:1:1 molar ratio. Signals assigned to 1-$C_{10}F_7MgEt$ or $C_6F_5MgEt$ were not detected.

### *4.20.1. 1-Heptafluoronaphthyl(pentafluorophenyl)magnesium*

$^{19}$F NMR (ether): δ = −107.30 (d, $^{3}J$(F$^{2}$, F$^{3}$) = 34 Hz, 1F, F$^{2}$), −144.26 (dd, $^{3}J$(F$^{8}$, F$^{7}$) = 16 Hz, $^{5}J$(F$^{8}$, F$^{5}$) = 16 Hz, 1F, F$^{8}$), −146.30 (d, $^{4}J$(F$^{4}$, F$^{5}$) = 56 Hz, 1F, F$^{4}$), −158.80 (t, $^{3}J$(F$^{para}$, F$^{meta}$) = 18 Hz, 1F, F$^{para}$), −148.0, −159.2, −161.8, −113.1, and −162.0 (1 F$^{5}$, 1 F$^{3}$, 1 F$^{6}$, 1 F$^{7}$, 2F$^{ortho}$, and 2F$^{meta}$, respectively).

### *4.21. Reaction of 2-$C_{10}F_7Br$ and $C_6F_5Br$ with ethylmagnesium bromide*

0.54 M EtMgBr in ether (1.6 mL, 0.86 mmol) was injected into solution of 2-$C_{10}F_7Br$ (108 mg, 0.32 mmol) and $C_6F_5Br$ (81 mg, 0.32 mmol) in ether (3 mL) and the solution was stirred at 22 °C for 2 h. The $^{19}$F NMR spectrum showed signals of 2-$C_{10}F_7MgBr$, (2-$C_{10}F_7)_2Mg$, $C_6F_5MgBr$, $(C_6F_5)_2Mg$ and, probably, 2-$C_{10}F_7MgC_6F_5$ in 10:2:10:2:2 molar ratio. Signals assigned to 1-$C_{10}F_7MgEt$ or $C_6F_5MgEt$ were not detected.

### *4.21.1. 2-Heptafluoronaphthyl(pentafluorophenyl))magnesium*

$^{19}$F NMR (ether): δ = −90.66 (dd, $^{4}J$(F$^{1}$, F$^{8}$) = 67 Hz, $^{5}J$(F$^{1}$, F$^{4}$) = 24 Hz, 1F, F$^{1}$), −108.26 (d, $^{3}J$(F$^{3}$, F$^{4}$) = 24 Hz, 1F, F$^{3}$), −145.6 (ddd, $^{4}J$(F$^{8}$, F$^{1}$) = 67 Hz, $^{3}J$(F$^{8}$, F$^{7}$) = 18 Hz, $^{5}J$(F$^{8}$, F$^{5}$) = 17 Hz, 1F, F$^{8}$), −149.05 (ddd, $^{4}J$(F$^{5}$, F$^{4}$) = 56 Hz, $^{3}J$(F$^{5}$, F$^{6}$) = 18 Hz, $^{5}J$(F$^{5}$, F$^{8}$) = 17 Hz, 1F, F$^{5}$), −153.3 (ddd, $^{4}J$(F$^{4}$, F$^{5}$) = 56 Hz, $^{5}J$(F$^{4}$, F$^{1}$) = 26 Hz, $^{3}J$(F$^{4}$, F$^{3}$) = 26 Hz, 1F, F$^{4}$), −158.36 (dd, $^{3}J$(F$^{6}$, F$^{7}$) = 18 Hz, $^{3}J$(F$^{6}$, F$^{5}$) = 14 Hz, 1F, F$^{6}$ or F$^{7}$), −161.45 (dd, $^{3}J$(F$^{7}$, F$^{8}$) = 18 Hz, $^{3}J$(F$^{7}$, F$^{6}$) = 18 Hz, 1F, F$^{7}$), −113.28 (m, 2F$^{ortho}$), −160.08 (t, $^{3}J$(F$^{para}$, F$^{meta}$) = 18 Hz, 1F$^{para}$), −162.0 (m, 2F$^{meta}$).

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jorganchem.2019.120889.

## References

[1] N.Y. Adonin, V.V. Bardin, U. Florke, H.J. Frohn, Z. Anorg. Allg. Chem. 631 (2005) 2638–2646.
[2] P.A. Morken, D.J. Burton, in: fourth ed., in: B. Baasner, H. Hagemann, J.C. Tatlow (Eds.), Houben-Weyl Methods of Organic Chemistry. Organo-Fluorine Compounds, 10b1, Thieme, Stuttgart, 2000, pp. 465–480. E10a.
[3] I.L. Knunyants, G.G. Yakobson (Eds.), Syntheses of Fluoroorganic Compounds, Springer., 1985, pp. 113–114.
[4] N.N. Vorozhtsov Jr., V.A. Barkhash, N.G. Ivanova, S.A. Anichkina, O.I. Andreevskaya, Dokl. Akad. Nauk SSSR 159 (1964) 125–128.
[5] (a) O.I. Osina, V.D. Shteingarts, J. Org. Chem. USSR 10 (1974) 329–334; (b) O.I. Osina, V.D. Shteingarts, Zh. Org. Khim. 10 (1974) 329–334.
[6] G.M. Brooke, J.M. Meara, J. Fluorine Chem. 50 (1990) 229–242.
[7] D.J. Morrison, S.D. Riegel, W.E. Piers, M. Parvez, R. McDonald, Chem. Commun. 27 (2006) 2875–2877.
[8] W.L. Respess, C. Tamborski, J. Organomet. Chem. 18 (1969) 263–274.
[9] L.T. Li, T.J. Marks, Organometallics 17 (1998) 3996–4003.
[10] J. Burdon, H.S. Gill, I.W. Parsons, J. Chem. Soc. Perkin Trans. 1 (1980) 2494–2496.
[11] J. Burdon, H.S. Gill, I.W. Parsons, J.C. Tatlow, J. Fluorine Chem. 24 (1984) 263–268.
[12] R.J. Harper, E.J. Soloski, C. Tamborski, J. Org. Chem. 29 (1964) 2385–2389.
[13] C. Tamborski, E.J. Soloski, J. Org. Chem. 31 (1966) 743–745.
[14] D.F. Evans, M.S. Khan, J. Chem. Soc. A (1967) 1643–1649.
[15] B. Gething, C.R. Patrick, J.C. Tatlow, J. Chem. Soc. (1962) 186–190.