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### An efficient stereoselective preparation of *cis*-perfluoroalkenylzinc reagents [(*E*)-R<sub>F</sub>CF=CFZnCl] by the metallation of 1*H*, 1*H*-perfluoroalkanes and their derivatization to *cis*-1-arylperfluoroalkenes [(*Z*)-R<sub>F</sub>CF=CFAr]

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#### Abstract

Various 1*H*,1*H*-perfluoroalkanes ( $R_FCF_2CH_2F$ ,  $R_F = CF_3$ ,  $C_2F_5$ ,  $C_4F_9$ ,  $C_5F_{11}$ ,  $C_6F_{13}$ ,  $C_{10}F_{21}$ ) were metallated using LDA in a THF solution of ZnCl<sub>2</sub> at RT or -78 °C to produce the corresponding perfluoroalkenylzinc reagents ( $R_FCF=CFZnCI$ ) in a *cis*-selective fashion. An increased yield (75–83%) and *cis*-selectivity (>89%) of the perfluoroalkenylzinc reagents were observed for metallation reactions performed at -78 °C. The *cis* selectivity was excellent for 1*H*,1*H*-perfluoroalkanes with larger  $R_F$  groups ( $C_4F_9$ ,  $C_5F_{11}$ ,  $C_6F_{13}$ , >96%). The *cis*-perfluoroalkenylzinc [(*E*)- $R_FCF=CFZnCI$ ] reagents were coupled with aryl iodides to obtain *cis*-1-arylperfluoroalkenes [(*Z*)- $R_FCF=CFArI$ ] in 71–95% isolated yields. The *cis*-perfluoroalkenylzinc reagents upon iodinolysis produced *cis*-1-iodoperfluoroalkenes [(*E*)- $R_FCF=CFI$ ] in 68–70% isolated yield. © 2006 Elsevier B.V. All rights reserved.

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#### 1. Introduction

Fluorinated alkenes are versatile synthetic building blocks because of their wide range of applications in the area of fluoropolymers, liquid crystalline materials and biologically active agents [1–3]. The physical and biological properties of alkenes largely depend on their configuration, and thus synthesis of polyfluorinated alkenes via an E or Z selective route would allow studies on the stereochemical, synthetic, kinetic, and biological aspects of fluorinated alkenes. But practical methods for the stereoselective synthesis of fluorinated alkenes remain as an important synthetic challenge. Various methodologies have been attempted for the stereoselective synthesis of different types of substituted fluorinated alkenes such as Horner-Wadsworth-Emmons reaction [4,5], addition-elimination of polyfluoroethenes [6,7], dehydrohalogenation [8], chlorofluorocarbene chemistry [9,10], radical reactions [11–13], chemistry involving ethyl phenylsulfinyl-

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fluoroacetate [14] or diethyl-2-oxo-3-fluorobutan-1,4-dioate [15], desulfenylation of  $\alpha$ -fluorosulfoxide [16–18], domino reaction based on an a normal Michael reaction [19], reduction of difluoroolefins [20,21], and fluorinated organometallics [22–29].

Recent investigations of Coe and co-workers realized the potential of hydrofluorocarbons HFC-134a and HFC-133a as a source for trifluorovinyllithium and chlorodifluorovinyllithium [30,31]. Based on this invention, we have developed excellent room temperature preparative methods for  $\alpha, \beta, \beta$ -trifluorostyrenes and  $\alpha$ -halo- $\beta$ , $\beta$ -diffuorostyrenes [32–37] via corresponding fluorovinylzinc reagents. In our methodology, the fluorovinylzinc reagents were generated at room temperature by an in situ metallation/transmetallation sequence followed by a Pd(0) catalyzed coupling reaction of the zinc reagents with aryl iodides to produce corresponding fluorostyrenes (Scheme 1) [32–37]. The metallation of hydrofluorocarbons at temperatures near room temperature was challenging as the intermediate fluorovinyllithiums are highly unstable (readily eliminate LiF) at a temperature typically above -78 °C. But by the systematic standardization of the reaction conditions and by performing the metallation in situ, the fluoroalkenylzinc

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Scheme 1. Synthesis of  $\alpha,\beta,\beta$ -trifluorostyrenes and  $\alpha$ -halo- $\beta,\beta$ -difluorostyrenes by metallation/coupling process.

reagents were generated in good yield via the corresponding lithium reagents at room temperature.

The success of this metallation methodology prompted us to test this strategy for a stereoselective synthesis of perfluoroalkenvlzinc reagents and 1-arylperfluoroalkenes from the corresponding 1H,1H-perfluoroalkane (R<sub>E</sub>CF<sub>2</sub>CH<sub>2</sub>F) precursors. 1-Arylperfluoroalkenes are not very well documented compounds and there are only a few methods available for their synthesis. especially in a stereoselective fashion. One of the early methods was developed by Dixon where reaction of phenyl lithium with perhaloalkenes produced 1-phenylsubstituted alkenes in 20-60% yields together with products formed by successive displacement of fluorines by phenyl groups [38]. Reaction of various substituted aryl Grignard reagents and hexafluoropropene were also reported in 40-50% yield for aryl-1,2,3,3,3pentafluoropropenes [39,40]. An improvement of the above reaction was reported by Dmowski, where an etheral solution of Grignard reagent was reacted with hexafluoropropene in a sealed tube [41]. Moreau et al. synthesized various 1substituted perfluoroalkenes from the reaction of perfluoroalkene (RFCF=CF<sub>2</sub>,  $R_F = C_6F_{13}$ ,  $C_4F_9$ ) with Grignard reagents [42,43]. All the above procedures produced the 1-arylperfluoroalkene as a mixture of E and Z isomers, favoring the Eisomer ( $E/Z \sim 80:20$ ). Dmowski [44–50] and Wakselman and co-workers [51] independently demonstrated that the geometry of the olefins affected the regiochemistry of the nucleophilic reaction of polyfluorinated propenes. Thus, the stereoselective synthesis of these alkenes was challenging and the first stereoselective preparation of (E)- and (Z)-1-phenylpentafluoropropenes were reported from our laboratory, where cis- and trans-1-iodopentafluoropropenes were transformed to the corresponding (E)- and (Z)-1-phenylpentafluoropropenes via zinc insertion followed by Pd(0) catalyzed coupling [52–54]. Kuroboshi and Hiyama et al. synthesized various (E)-1-arylperfluoropropenes by dehydrohalogenation of the corresponding precursor using DBU [55]. Excellent E selectivity was observed in this dehydrohalogenation. They have also obtained the Z-isomer of the above alkenes by a photochemical isomerization reaction. We have very recently developed a

Scheme 2. Synthesis of 1-arylperfluoroalkenes by dehydrofluorination of suitable precursors.

similar dehydrofluorination method for the synthesis of (E)-1-phenyl-1,2,3,3,3-pentafluoropropene and (E)-1-aryl-1,2,2,3,3,4,4,4-octafluorobutene by the dehydrofluorination of the corresponding precursor using lithium hexamethyldisilazide base [56,57]. Excellent *E*-selectivity was observed during this dehydrofluorination process (Scheme 2).

Thus the synthesis of (E)-R<sub>F</sub>CF=CFAr in good selectivity was possible either by the organometallic or dehydrohalogenation methods discussed above whereas the corresponding Zisomer was difficult to obtain by any of these methods. The preparation of 1-arylperfluoroalkenes via the corresponding zinc reagent followed by Pd(0) coupling utilized pure cis- or trans-1-iodo-perfluoroalkene (R<sub>F</sub>CF=CFI). The precursor for the *trans*-iodide,  $[(Z)-R_FCF=CHF]$  could be obtained via the stereospecific phosphodefluoridation of the readily available perfluoro-1-alkene (R<sub>F</sub>CF=CF<sub>2</sub>) [58-61]. The corresponding precursors for the *cis*-iodide,  $[(E)-R_FCF=CHF]$  are less conveniently available than the *trans*-isomers. They have been synthesized by the isomerization of (Z)- $R_FCF$ =CHF ( $R_F = CF_3$ ,  $C_2F_5$ -) using SbF<sub>5</sub> [58,62], but this methodology was not feasible for perfluoroalkenes with longer chains due to the formation of internal isomers in addition to the desired product [63]. So the synthesis of (Z)-1-arylperfluoroalkenes is rather difficult and it is useful to develop a methodology that would generate them exclusively in good yield.

#### 2. Results and discussion

Recently, Frohn et al. reported metallation of C<sub>6</sub>F<sub>13</sub>CF<sub>2</sub>CH<sub>2</sub>F with 2 equiv. BuLi under conditions similar to that of the metallation of HFC-134a [30,31] at low temperature to produce the corresponding perfluoroalkenyllithium ( $C_6F_{13}CF=CFLi$ ) in a *cis*-selective fashion (Scheme 3) [64,65]. Here the initially formed intermediate lithium species  $[C_6F_{13}CF_2CHFLi]$  eliminates LiF and leads to the (Z)-C<sub>6</sub>F<sub>13</sub>CF=CHF with 95% selectivity, which was then readily consumed by the base to produce the perfluoroalkenyllithium species. The perfluoroalkenvllithium species thus generated was then successfully transformed to potassium cis-perfluoroocten-1-yltrifluoroborate ( $K[C_6F_{13}CF=CFBF_3]$ ) by treatment with B(OCH<sub>3</sub>)<sub>3</sub> followed by K[HF<sub>2</sub>] and aqueous HF.

The excellent *cis*-selectivity described in this elimination prompted us to investigate a similar process to produce the corresponding *cis*-perfluoroalkenylzinc reagents [(*E*)- $R_FCF=C$ FZnCl] via our in situ metallation strategy. The *cis*perfluoroalkenylzinc reagents thus generated could be effectively used in a coupling reaction with aryl iodides to produce *cis*-1-arylperfluoroalkylolefins [(*Z*)- $R_FCF=CFAr$ ], and thus

$$C_{6}F_{13}CF_{2}CH_{2}F \xrightarrow{2 \text{ BuLi}}_{-75 \text{ °C, THF}} [C_{6}F_{13}CF=CFLi] \xrightarrow{B(OMe)_{3}} \text{ Li}[C_{6}F_{13}CF=CFB(OMe)_{3}] + C_{6}F_{13}CF=CFB(OMe)_{2}$$

$$K[HF_{2}] \downarrow MeOH, H_{2}O, \text{ aq. HF}$$

$$K[C_{6}F_{13}CF=CFBF_{3}]$$

Scheme 3. Preparation of cis-perfluoroocten-1-yltrifluoroborate via corresponding cis-perfluoroalkenyl lithium.

serve as a general methodology for the preparation of these olefins in a stereoselective fashion.

### 2.1. Synthesis of cis-perfluoroprop-1-enylzinc reagent [(E)-CF<sub>3</sub>CF=CFZnCl] and (Z)-1-arylperfluoroprop-1-enes [(Z)-CF<sub>3</sub>CF=CFAr]

Firstly, commercially available 1H,1H-perfluoropropane (CF<sub>3</sub>CF<sub>2</sub>CH<sub>2</sub>F) was chosen and its metallation was performed with 2 equiv. of LDA in the presence of ZnCl<sub>2</sub> at 15 °C [32,33] to produce the corresponding perfluoropropenylzinc reagent (CF<sub>3</sub>CF=CFZnCl) in 67% yield. <sup>19</sup>F NMR analysis of the reaction mixture showed that perfluoropropenylzinc reagent was formed as a mixture of isomers with 82:18 selectivity in favor of the *cis*-isomer. The Pd(0) catalyzed coupling reaction of this zinc reagent with 4-fluoroiodobenzene produced 1-(4fluorophenyl)perfluoroprop-1-ene in 78% isolated yield with similar stereoselectivity (Z/E 81:19) observed for the zinc reagent. In order to improve the yield and *cis*-selectivity we have carried out the metallation reaction at -78 °C. <sup>19</sup>F NMR analysis of the reaction mixture revealed an improved yield (81%) and *cis*-selectivity ((E/Z)-CF<sub>3</sub>CF=CFZnCl = ~89:11) of the zinc reagent. The ratio of the mono and bis zinc reagents in the THF medium was not clear, but addition of 1 equiv. of TMEDA to the reaction medium clearly showed distinct peaks for the mono and bis zinc reagents complexed to TMEDA (mono/bis =  $\sim$ 70:30). We then attempted the metallation reaction using a more sterically hindered base in order to push the selectivity further. Thus, the metallation reaction was performed using lithium tetramethyl-4-methoxy piperidine (4methoxy LiTMP) at -78 °C, but no improvement in the selectivity was observed (*E*/*Z* 89:11). Formation of the perfluoropropenylzinc reagent was established by a hydrolysis experiment where the zinc reagent obtained by the metallation reaction was treated with acetic acid to obtain the corresponding (*Z*)- and (*E*)-CF<sub>3</sub>CF=CFH with the retention of selectivity of the zinc reagent (*Z*/*E* 87:13). A metallation reaction using 1 equiv. of LDA at -80 °C was also attempted but produced only a 34% yield of the perfluoroalkenylzinc reagent along with unreacted alkane CF<sub>3</sub>CF<sub>2</sub>CH<sub>2</sub>F. No intermediate alkene (CF<sub>3</sub>CF=CHF) was detected in this reaction mixture confirming that the proton in CF<sub>3</sub>CF=CHF is more acidic than that of the precursor alkane (CF<sub>3</sub>CF<sub>2</sub>CH<sub>2</sub>F) which was readily consumed by the base as soon as it was formed.

After obtaining the perfluoroalkenylzinc reagent in good yield and *cis*-selectivity we have performed the Pd(0) catalyzed coupling reaction of the zinc reagent mixture with various aryl iodides. The reaction proceeded well with aryl iodides having both electron donating and withdrawing groups in the aromatic ring to produce the corresponding 1-arylperfluoroopropenes in excellent isolated yield. The configuration of the zinc reagent was retained during the coupling process to produce the *cis*-1-arylperfluoropropenes as the major isomer. The result of coupling reaction of the *cis*-perfluoroprop-1-enylzinc reagent (prepared at -78 °C) with aryl iodides is summarized in Table 1. The *Z* and *E* isomers were very close in their  $R_{\rm F}$  values and were isolated as mixtures by column chromatography using hexanes as eluent.

Table 1

Pd(0) catalyzed coupling reaction of perfluoropropenylzinc reagent (prepared at -78 °C) with any iodides: synthesis of (Z)-1-anylperfluoroprop-1-enes

$$CF_{3}CF_{2}CH_{2}F \xrightarrow{LDA, ZnCl_{2}} F_{3}C \xrightarrow{F} F_{2}C$$

$$\xrightarrow{F_{3}C} ZnCl \xrightarrow{Arl, 65 °C} F_{3}C \xrightarrow{F} F_{3}C$$

$$\xrightarrow{15 °C, 67\%, E/Z = 82:18} -78 °C, 80\%, E/Z = 89:11$$

Entry	Ar	Time (h)	Yield (%) of ArCF=CFCF <sub>3</sub>	Z/E ratio <sup>a</sup>
1	C <sub>6</sub> H <sub>5</sub> -	8	80	87:13
2	$4-FC_6H_4$	8	77	87:13
3	$2-CH_3C_6H_4-$	10	87	89:11
4	3-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> -	6	78	90:10
5	$3-CF_3C_6H_4-$	8	82	88:12

<sup>a</sup> The Z/E ratio determined by <sup>19</sup>F NMR ( ${}^{3}J_{FF(trans)} = \sim 131$  Hz,  ${}^{3}J_{FF(cis)} = \sim 12$  Hz).

Table 2

Pd(0) catalyzed coupling reaction of the perfluorobutenylzinc reagent (prepared at -78 °C) with aryl iodides: synthesis of (Z)-1-arylperfluorobut-1-enes

$$C_{2}F_{5}CF_{2}CH_{2}F \xrightarrow{LDA, ZnCl_{2}} \left[ \begin{array}{c} F \\ C_{2}F_{5} \end{array} \right] \xrightarrow{F} ZnCl \\ THF \end{array} \xrightarrow{F} ZnCl \\ 15 \ ^{\circ}C, \ 61\%, \ E/Z = 86:14 \\ -78 \ ^{\circ}C, \ 76\%, \ E/Z = 94:6 \end{array} \xrightarrow{F} C_{2}F_{5} \xrightarrow{F} Ar$$

Entry	Ar	Time (h)	Yield (%) of ArCF=CFC <sub>2</sub> F <sub>5</sub>	Z/E ratio <sup>a</sup>
1	C <sub>6</sub> H <sub>5</sub> -	6	89	93:7
2	$4-FC_6H_4$	5	81	94:6
3	2-(CH <sub>3</sub> ) <sub>2</sub> CHC <sub>6</sub> H <sub>4</sub> -	18	71	94:6
4	$3-CF_3C_6H_4-$	8	83	93:7

<sup>a</sup> The Z/E ratio determined by <sup>19</sup>F NMR ( ${}^{3}J_{FF(trans)} = \sim 133$  Hz,  ${}^{3}J_{FF(cis)} = \sim 11$  Hz).

# 2.2. Synthesis of cis-perfluorobut-1-enylzinc reagent $[(E)-C_2F_5CF=CFZnCl]$ and (Z)-1-arylperfluorobut-1-enes $[(Z)-C_2F_5CF=CFAr]$

After the successful preparation of (Z)-1-arylperfluoroprop-1-enes from 1H,1H-perfluoropropane we have attempted a similar sequence of experiments for the commercially available higher homologue 1H,1H-perfluorobutane (C<sub>2</sub>F<sub>5</sub>CF<sub>2</sub>CH<sub>2</sub>F). Metallation of C<sub>2</sub>F<sub>5</sub>CF<sub>2</sub>CH<sub>2</sub>F in the presence of ZnCl<sub>2</sub> at 15 °C in THF solvent produced the corresponding perfluorobut-1enylzinc reagent (C<sub>2</sub>F<sub>5</sub>CF=CFZnCl) in 61% yield. <sup>19</sup>F NMR analysis revealed that a slightly improved selectivity (E/Z)86:14) was obtained in comparison to that of the perfluoropropenylzinc reagent preparation under similar conditions. The metallation reaction was then performed at -78 °C in THF medium in the presence of ZnCl<sub>2</sub> and the <sup>19</sup>F NMR revealed that the perfluorobutenylzinc reagent was formed in 76% yield with an improved selectivity towards the *cis*-isomer ((E/Z)- $C_2F_5CF=CFZnCl = \sim 94:6$ ). Addition of 1 equiv. of TMEDA to this zinc reagent mixture clearly showed distinguishable peaks for the mono and bis zinc reagents (mono/bis =  $\sim 65:35$ ). Palladium catalyzed cross-coupling of this zinc reagent with various aryl iodides (having both electron donating and withdrawing groups in the aromatic ring) was then attempted and produced the 1-arylperfluorobutenes in excellent isolated yield. The results of the coupling reaction of perfluorobutenylzinc reagent (prepared at -78 °C) with anyl iodides are summarized in Table 2. The cis-configuration remained intact

during the coupling process and no isomerization was observed. For a sterically hindered *ortho* substituent, 2-isopropyl, the coupling reaction was sluggish (entry 3), and after 18 h at 65  $^{\circ}$ C, furnished 71% isolated yield of the coupled product.

#### 2.3. Synthesis of 1H,1H-perfluoroalkanes

The improvement in the *cis*-stereoselectivity during the metallation of  $C_2F_5CF_2CH_2F$  in comparison to  $CF_3CF_2CH_2F$  indicates that there is some influence by the larger perfluoroethyl group during the course of the key elimination process (see Section 2.7). This prompted us to consider 1*H*,1*H*perfluoroalkanes with even larger  $R_F$  groups, such as  $C_4F_9$ ,  $C_5F_{11}$ ,  $C_6F_{13}$ ,  $C_{10}F_{21}$  for this metallation process. So four 1*H*,1*H*-perfluoroalkanes ( $R_FCF_2CH_2F$ ,  $R_F = C_4F_9$ ,  $C_5F_{11}$ ,  $C_6F_{13}$ ,  $C_{10}F_{21}$ ) were prepared from the corresponding alcohol (Scheme 4) [64]. The precursor alcohols ( $R_FCF_2CH_2OH$ ) were either commercially available or synthesized by the room temperature reduction of the methyl ester of the corresponding acids ( $R_FCF_2CO_2Me$ ) using NaBH<sub>4</sub> [66].

# 2.4. Synthesis of cis-perfluorohex-1-enylzinc reagent $[(E)-C_4F_9CF=CFZnCl]$ and (Z)-1-arylperfluorohex-1-ene $[(Z)-C_4F_9CF=CFAr]$

Metallation of  $C_4F_9CF_2CH_2F$  was performed using LDA in the presence of ZnCl<sub>2</sub> under the standard reaction conditions (-78 °C in THF) to obtain the corresponding perfluorohex-1enylzinc reagent [ $C_4F_9CF=CFZnCl$ ] in 75% yield with excellent *cis*-selectivity (*E/Z* 96:4). The <sup>19</sup>F NMR spectrum of the zinc reagent mixture was complex to determine the *mono* and *bis* ratio, but addition of 1 equiv. of TMEDA made it relatively simple indicating a 70:30 mixture of the *mono* and *bis* zinc reagents. Palladium catalyzed cross-coupling reaction of the zinc reagent with various aryl iodides was then performed and the reaction yielded 1-arylperfluorohexenes in excellent isolated yield (78–81%) and *cis*-selectivity (>95%). The results of the coupling reaction of perfluorohex-1-enylzinc reagent with various aryl iodides are summarized in Table 3.

# 2.5. Synthesis of cis-perfluorohept-1-enylzinc reagent $[(E)-C_5F_{11}CF=CFZnCl]$ and (Z)-1-arylperfluorohept-1-enes $[(Z)-C_5F_{11}CF=CFAr]$

The metallation of  $C_5F_{11}CF_2CH_2F$  was then attempted both at 0 and at -78 °C with 2 equiv. of LDA in presence of ZnCl<sub>2</sub>. At 0 °C, the reaction produced 75% of the perfluorohept-1-

$$R_{F}CF_{2}CH_{2}OH \xrightarrow{C_{4}F_{9}SO_{2}F} R_{F}CF_{2}CH_{2}OSO_{2}C_{4}F_{9} \xrightarrow{KF, TG} R_{F}CF_{2}CH_{2}F$$

$$0^{\circ}C-rt, >95\% R_{F}CF_{2}CH_{2}OSO_{2}C_{4}F_{9} \xrightarrow{KF, TG} R_{F}CF_{2}CH_{2}F$$

$$R_{F} = n-C_{4}F_{9}, 68\%$$

$$n-C_{5}F_{11}, 71\%$$

$$n-C_{6}F_{13}, 69\%$$

$$n-C_{10}F_{21}, 87\%$$

460 Table 3

Pd(0) catalyzed coupling reaction of the perfluorohex-1-enylzinc reagent with aryl iodides: synthesis of (Z)-1-arylperfluorohex-1-enes



Entry	Ar	Time (h)	Yield (%) of ArCF=CFC <sub>4</sub> F <sub>9</sub>	Z/E ratio <sup>a</sup>
1	C <sub>6</sub> H <sub>5</sub> -	8	81	96:4
2	2-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> -	15	81	96:4
3	$4-CH_3OC_6H_4-$	6	79	96:4
4	$3-CF_3C_6H_4-$	8	78	95:5

<sup>a</sup> The Z/E ratio determined by <sup>19</sup>F NMR ( ${}^{3}J_{FF(trans)} = \sim 132$  Hz,  ${}^{3}J_{FF(cis)} = \sim 12$  Hz).

envlzinc reagent  $[C_5F_{11}CF=CFZnCl]$  with good *cis*-selectivity (E/Z 88:12). Palladium catalyzed coupling reaction of the zinc reagent with iodobenzene produced the 1-phenylperfluoroheptene with similar selectivity (Z/E 87:13). When the reaction was performed at -78 °C, an 83% yield of the zinc reagent was formed with exclusive formation of the *cis*-isomer (E/Z, 99:1). Pd(0) catalyzed coupling reaction of the perfluoroheptenylzinc reagent (prepared at -78 °C) with various aryl halides was then performed and the results are summarized in Table 4. The coupling reaction was equally good for aryl iodides with both electron donating or withdrawing groups in the aromatic ring to afford a series of (Z)-1-arylperfluoroheptenes almost exclusively as a single isomer. With 2-methyl-6-nitroiodobenzene, the reaction was sluggish, but heating for 32 h produced the coupled product in 31% isolated yield (Table 4, entry 3). The ratio of the cis- and trans-1-(2-methyl-6-nitrophenyl)perfluoroheptene (91:9) formed in this reaction differed from that of the starting perfluoroheptenylzinc reagent (99:1). This observation indicates either isomerization or a preferred reactivity of the *trans*-perfluoroheptenylzinc reagent during this sluggish coupling reaction.

# 2.6. Synthesis of cis-perfluorooct-1-enylzinc reagent $[(E)-C_6F_{13}CF=FZnCl]$ and (Z)-1-arylperfluorooct-1-enes $[(Z)-C_6F_{13}CF=CFAr]$

Metallation of C<sub>6</sub>F<sub>13</sub>CF<sub>2</sub>CH<sub>2</sub>F was performed at -78 °C with 2 equiv. of LDA in presence of ZnCl<sub>2</sub> to obtain 79% yield of the zinc reagent. The <sup>19</sup>F NMR analysis revealed that the *cis*-isomer was formed almost exclusively (*E/Z*, 98:2). It was difficult to assign peaks for the *mono* and *bis* zinc reagent species even with the addition of TMEDA. Palladium catalyzed coupling reaction of the *cis*-perfluorooct-1-enylzinc reagent with various aryl iodides was then performed and we obtained the corresponding *cis*-1-arylperfluorooctenes in very good isolated yield. The results of the coupling reaction of perfluorooct-1-enylzinc reagent with aryl iodides are summarized in Table 5.

Table 4

Pd(0) catalyzed coupling reaction of the perfluoroheptenylzinc reagent (prepared at -78 °C) with anyl iodides: synthesis of (Z)-1-arylperfluorohept-1-enes

$$n-C_{5}F_{11}CF_{2}CH_{2}F \xrightarrow{LDA, ZnCl_{2}} \left[ \begin{array}{c} F \\ n-C_{5}F_{11} \\ r-C_{5}F_{11} \\ r-C_$$

Entry	Ar	Time (h)	Yield (%) of ArCF=CFC <sub>5</sub> F <sub>11</sub>	Z/E ratio <sup>a</sup>
1	C <sub>6</sub> H <sub>5</sub> -	8	89	99:1
2	$4-FC_6H_4$	12	91	99:1
3 <sup>b</sup>	2-CH <sub>3</sub> (6-NO <sub>2</sub> )C <sub>6</sub> H <sub>3</sub> -	32	31	91:9
4	$4-CH_3OC_6H_4-$	8	92	98:2
5	$3-CF_3C_6H_4-$	6	86	98:2

<sup>a</sup> The Z/E ratio determined by <sup>19</sup>F NMR ( ${}^{3}J_{FF(trans)} = \sim 132$  Hz,  ${}^{3}J_{FF(cis)} = \sim 11$  Hz).

<sup>b</sup> Product olefin was contaminated with traces of 2-methyl-6-nitroiodobenzene.

Table 5

Pd(0) catalyzed coupling reaction of the perfluorooct-1-enylzinc reagent with aryl iodides: synthesis of (Z)-1-arylperfluorooct-1-enes



Entry	Ar	Time (h)	Yield (%) of ArCF=CFC <sub>6</sub> $F_{13}$	Z/E ratio <sup>a</sup>
1	C <sub>6</sub> H <sub>5</sub> -	6	81	98:2
2	$4-FC_6H_4-$	15	91	97:3
3	$2-CH_3C_6H_4-$	18	78	98:2
4	$4-CH_3OC_6H_4-$	8	87	98:2
5	$3-CF_{3}C_{6}H_{4}-$	10	95	98:2

<sup>a</sup> The Z/E ratio determined by <sup>19</sup>F NMR ( ${}^{3}J_{FF(trans)} = \sim 131$  Hz,  ${}^{3}J_{FF(cis)} = \sim 12$  Hz).

# 2.7. Synthesis of cis-perfluorododec-1-enylzinc reagent $[(E)-C_{10}F_{21}CF=CFZnCl]$ and (Z)-1-arylperfluorododec-1-enes $[(Z)-C_{10}F_{21}CF=CFAr]$

Metallation of a 1H,1H-perfluorododecane ( $C_{10}F_{21}CF_2$  CH<sub>2</sub>F) was also attempted in THF or a THF-diethyl ether solution at -78 °C. But, unfortunately, the reaction did not proceed well at -78 °C due to the poor solubility of  $C_{10}F_{21}CF_2CH_2F$  in THF or THF-diethyl ether. The reaction was then performed at 0 °C in the THF-diethyl ether medium and produced the perfluorododec-1-enylzinc reagent in 61% yield but with a slightly diminished selectivity towards the *cis* isomer ( $E/Z \sim 93:7$ ). The palladium catalyzed cross-coupling reaction of the perfluorododec-1-enylzinc reagent with various aryl iodides was then performed and the reaction produced 1-arylperfluorododecenes in good yield (72–81%) and *cis*-selectivity (>92%). The results of the coupling reaction of perfluorododec-1-enylzinc reagent with aryl iodides are summarized in Table 6.

#### 2.8. Stereochemistry of the olefination

The excellent *cis*-selectivity observed during the metallation of  $R_FCF_2CH_2F$  could be explained by looking at the *syn*-clinal and anti-periplanar conformations of R<sub>F</sub>CF<sub>2</sub>CH<sub>2</sub>F. On the basis of spectral data and theoretical calculations it was established that the syn-clinal conformations are favored over the antiperiplanar conformations for 1,2-difluoroethanes despite the dipole or steric repulsion resulting from electronegative gauche fluorine atoms [67]. It was also established that the syn-clinal effect is due to the relatively large electron flow from the  $\sigma_{C-H}$ bond towards to the  $\sigma^*_{C-F}$  relative to the electron flow from  $\sigma_{C-F}$ bond to the  $\sigma^*_{C-F}$  bond in the *anti*-periplanar conformation [67]. Based on similar facts, 1H,1H-perfluoroalkanes adopts more stable syn-clinal conformation (Fig. 1A) relative to the less favorable anti-periplanar confirmation (Fig. 1B) despite having steric or repulsive interactions resulting from the electronegative gauche fluorine atoms. The attack of the base on the more favored syn-clinal conformation results in the lithiated mono anion (R<sub>F</sub>CF<sub>2</sub>CHFLi), which internally eliminates LiF to produce the *cis*-alkene as the preferred isomer during the metallation process. Additionally, the anti-periplanar confirmation (B) is destabilized by the significant steric as well as electronic repulsive interaction between the gauche R<sub>F</sub> group and F thus favoring A as the preferred conformation [68]. Thus more bulky the  $R_F$  group in the 1H,1H-perfluoroalkenes, the higher the ratio of *cis*-isomer during the metallation process.

Table 6

Pd(0) catalyzed coupling reaction of the perfluorododec-1-enylzinc reagent with aryl iodides: synthesis of (Z)-1-arylperfluorododec-1-enes

Entry	Ar	Time (h)	Yield (%) <sup>a</sup> of ArCF=CFC <sub>10</sub> F <sub>21</sub>	Z/E ratio <sup>b</sup>
1	C <sub>6</sub> H <sub>5</sub> -	12	78	94:6
2	$4-CH_3OC_6H_4-$	10	76	93:7
3	4-F C <sub>6</sub> H <sub>4</sub> -	12	72	92:8
4	$3-CF_3C_6H_4-$	12	81	93:7

<sup>a</sup> The product olefin was contaminated with traces of  $C_{10}F_{21}CF_2CH_2F$  and Z- $C_{10}F_{21}CF$ =CHF.

<sup>b</sup> The Z/E ratio determined by <sup>19</sup>F NMR ( ${}^{3}J_{FF(trans)} = \sim 130$  Hz,  ${}^{3}J_{FF(cis)} = \sim 10$  Hz).



Fig. 1. Syn-clinal and anti-periplanar conformations of R<sub>E</sub>CF<sub>2</sub>CH<sub>2</sub>F. The more stable syn-clinal form (A) results in the cis-alkene during the metallation process.

#### 2.9. Synthesis of cis-1-iodoperfluoroalkenes

We also extended this methodology for a convenient synthesis of cis-1-iodoperfluoroalkenes. Trans-1-iodo-perfluoroalkenes ((Z)- $R_FCF=CFI$ ) are well known and are prepared either by metallation of the (E)-R<sub>F</sub>CF=CFH, followed by iodinolysis [69,70] or thermal decomposition of the perfluoroalkyl Grignard reagents [71,72]. However, the cis-1-iodoperfluoroalkenes ((E)-R<sub>F</sub>CF=CFI) are less conveniently available and more difficult to synthesize, especially the higher homologues [the higher homologues other than  $R_F = CF_3$ , C<sub>2</sub>F<sub>5</sub>] cannot be prepared by the SbF<sub>5</sub> catalyzed isomerization of ((E)-R<sub>F</sub>CF=CFH) [58,62,63]. Iodinolysis of the cisperfluoroalkenylzinc reagent generated by our in situ metallation method could eventually give to the corresponding cis-1iodo-perfluoroalkenes. Thus, the perfluoroalkenylzinc reagents generated by the metallation of 1H,1H-perfluoroheptene and 1H,1H-perfluorooctene at -78 °C were treated with iodine at 0 °C to produce the 1-iodoperfluoroheptene and 1-idodoperfluorooctene in 68% and 70% isolated yields, respectively, with >98% cis-selectivity (Scheme 5).

In conclusion, a stereoselective synthesis of *cis*-perfluoroalkenenylzinc reagents ([R<sub>F</sub>CF=CFZnCl], R<sub>F</sub> = CF<sub>3</sub>, C<sub>2</sub>F<sub>5</sub>, C<sub>4</sub>F<sub>9</sub>, C<sub>5</sub>F<sub>11</sub>, C<sub>6</sub>F<sub>13</sub>, C<sub>10</sub>F<sub>21</sub>) was achieved by metallation of 1*H*,1*H*-perfluoroalkanes at low temperature. Temperature and size of the R<sub>F</sub> group influenced the selectivity in the elimination process. A *cis*-selectivity >96% was observed for 1*H*,1*H*perfluoroalkanes with larger R<sub>F</sub> groups (C<sub>4</sub>F<sub>9</sub>, C<sub>5</sub>F<sub>11</sub>, C<sub>6</sub>F<sub>13</sub>) when the metallation was performed at -78 °C. The *cis*perfluoroalkenenylzinc reagents coupled with aryl iodides under palladium catalysis to produce *cis*-1-arylperfluoroalkenes in excellent isolated yield. The *cis*-perfluoroalkenenylzinc reagents were also subjected to iodinolysis to afford *cis*-1iodoperfluoroalkenes ((*E*)- $R_FCF=CFI$ ) in excellent isolated yield. Overall this methodology serves as the first general route for the synthesis of the relatively difficult *cis*-1-arylperfluoroalkenes and *cis*-1-iodoperfluoroalkenes.

#### 3. Experimental

<sup>1</sup>H and <sup>19</sup>F NMR spectra were recorded on a Brucker AC-300 or a WM 360 or a DRX 400 Spectrometer. Chemical shifts have been reported in ppm relative to an internal reference (CDCl<sub>3</sub>, CFCl<sub>3</sub> or TMS). Unless noted otherwise, CDCl<sub>3</sub> was used as the NMR lock solvent. Yields of the perfluoroalkenylzinc reagent were calculated based on ZnCl<sub>2</sub>. All the <sup>19</sup>F NMR yields were calculated based on PhCF<sub>3</sub> as an internal standard. All Z/E ratios of the perfluoroalkenylzinc reagents or 1-arylperfluoroalkenes were determined based on <sup>19</sup>F NMR coupling constants of the fluorine attached to the double bond  $({}^{3}J_{FF(trans)} = \sim 130 \text{ Hz}, {}^{3}J_{FF(cis)} = \sim 11 \text{ Hz}).$  Isolated yields of the 1-arylperfluoroalkenes were based on aromatic iodide. Low resolution mass spectra were obtained using a Voyeger GC/MS instrument operated at 70 eV in the electron impact mode, using a 15 m CB-5 column. The reported fragment peaks correspond to the most abundant ions, in addition to the parent ion(s). Highresolution mass spectra (HRMS) were obtained by the University of Iowa High Resolution Mass Spectrometry Facility. Column chromatography was carried out using silica gel purchased from Em Science (Silica Gel 60, particle size

$$R_{F}CF_{2}CH_{2}F \xrightarrow{LDA, ZnCl_{2}} \left[ \begin{array}{c} F \\ R_{F} \end{array} \right] \xrightarrow{F} ZnCl \left[ \begin{array}{c} I_{2} \\ 0 \ ^{\circ}C \end{array} \right] \xrightarrow{F} F_{R_{F}} \xrightarrow{F} I$$

$$R_{F} = n \cdot C_{5}F_{11}, 68\%, E/Z 98:2$$

$$R_{F} = n \cdot C_{6}F_{12}, 70\%, E/Z 99:1$$

Scheme 5. Synthesis of cis-1-iodoperfluoroalkenes.

63–200  $\mu$ m). All boiling points were measured during distillation and are uncorrected. Tetrahydrofuran (THF), diethylether and triglyme (TG) were dried by distillation from sodium benzophenone/ketyl at atmospheric pressure immediately prior to use. Pd(PPh<sub>3</sub>)<sub>4</sub> was prepared by Coulson's procedure [73]. N<sub>2</sub> was used without further purification. All other reagents and chemicals were obtained from commercial sources and used directly.

#### 3.1. Synthesis of 1H,1H-perfluoroalkanes

#### 3.1.1. 1H,1H-Perfluorohexane $(C_5F_{11}CH_2F)$

solution of 1H,1H-perfluorohexan-1-ol (5.0 g, А 16.7 mmol) and triethylamine (1.85 g, 18.3 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10.0 mL) was cooled to  $0^{\circ}$ C and perfluorobutanesulfonyl fluoride (6.04 g, 19.9 mmol) was added dropwise with stirring. The reaction mixture was stirred at RT for 3 h and volatile products and CH<sub>2</sub>Cl<sub>2</sub> removed under vacuum and the residue dissolved in ether (40 mL) and washed many times with water and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. Removal of the solvent produced pure 1H,1H-perfluorohexenylnonaflate as a viscous liquid (8.91 g, 15.3 mmol, 92%) [<sup>19</sup>F NMR (CDCl<sub>3</sub>):  $\delta$  -81.2 (t, J = 11 Hz, 3F), -81.3 (t, J = 11 Hz, 3F), -110.2 (t, J = 15 Hz, 2F), -120.2 (m, 2F), -121.6 (m, 2F), -123.3(m, 2F), -123.6 (m, 2F), -126.4 (m, 2F), -126.7 (m, 2F).NMR (CDCl<sub>3</sub>):  $\delta$  4.88 (t, J = 12 Hz, 2H)].

The 1*H*,1*H*-perfluorohexylnonaflate (10.3 g, 17.7 mmol) and KF (5.13 g, 88.5 mmol) were stirred in triglyme (TG) (98.0 mL) at 180–200 °C for 3 h and the volatile products distilled out during this period. The distillate was washed with water (3×10 mL) and the organic layer dried over CaH<sub>2</sub> and distilled to obtain pure 1*H*,1*H*-perfluorohexane as a colorless liquid (3.65 g, 12.0 mmol) in 68% yield [bp: 82–83 °C]. <sup>19</sup>F NMR (CDCl<sub>3</sub>):  $\delta$  –81.3 (t, *J* = 11 Hz, 3F), –123.3 (m, 2F), –123.6 (m, 2F), –124.5 (m, 2F), –126.7 (m, 2F), –242.2 (tm, *J* = 46 Hz, 1F). <sup>1</sup>H NMR (CDCl<sub>3</sub>): 4.75 (dt, *J* = 46, 12 Hz, 2H).

#### 3.1.2. 1H,1H-Perfluoroheptane $(C_6F_{13}CH_2F)$

By a similar procedure, 1*H*,1*H*-perfluoroheptan-1-ol (32.0 g, 91.4 mmol) was treated with triethylamine (11.07 g, 109.6 mmol) and perfluorobutanesulfonyl fluoride (35.8 g, 118.8 mmol) to obtain 1*H*,1*H*-perfluoroheptylnonaflate as a white crystalline solid (56.1 g, 88.8 mmol, 97%) [mp: 34–35 °C]. <sup>19</sup>F NMR (CDCl<sub>3</sub>):  $\delta$  –81.2 (t, *J* = 11 Hz, 3F), -81.3 (t, *J* = 9 Hz, 3F), -110.2 (t, *J* = 12 Hz, 2F), -120.1 (m, 2F), -121.7 (m, 2F), -122.4 (m, 2F), -123.3 (m, 4F), -126.3 (m, 2F), -126.6 (m, 2F). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  4.84 (t, *J* = 12 Hz, 2H).

1*H*,1*H*-Perfluoroheptylnonaflate (25.0 g, 39.6 mmol) was treated with KF (11.4 g, 197.8 mol) in TG (200 mL) at 200 °C for 5 h, followed by isolation as per the above procedure to afford 1*H*,1*H*-perfluoroheptane as a colorless liquid (9.85 g, 28.0 mmol, 71%) [bp: 108–110 °C]. <sup>19</sup>F NMR (CDCl<sub>3</sub>): δ –81.4 (t, *J* = 11 Hz, 3F), –122.8 (m, 2F), –123.3 (m, 4F), –124.3 (m, 2F), –126.7 (m, 2F), –242.2 (tm, *J* = 46 Hz, 1F). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 4.75 (dt, *J* = 46, 12 Hz, 2H).

#### 3.1.3. 1H,1H-Perfluorooctane $(C_7F_{15}CH_2F)$

By a similar procedure 1*H*,1*H*-perfluorooctan-1-ol (15.2 g, 38.0 mmol) was treated with triethylamine (4.60 g, 45.6 mmol) and perfluorobutanesulfonyl fluoride (14.92 g, 49.4 mmol) to obtain 1*H*,1*H*-perfluorooctylnonaflate as a white crystalline solid (24.9 g, 36.5 mmol, 96%) [64] [mp: 42–44 °C]. <sup>19</sup>F NMR (CDCl<sub>3</sub>):  $\delta$  –81.1 (t, *J* = 10 Hz, 3F), –81.2 (t, *J* = 10 Hz, 3F), –110.2 (t, *J* = 12, 2F), –120.1 (m, 2F), –121.6 (m, 2F), –122.3 (m, 4F), –123.3 (m, 4F), –126.3 (m, 2F), –126.6 (m, 2F). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  4.89 (t, *J* = 12 Hz, 2H).

1*H*,1*H*-Perfluorooctylnonaflate (23.3 g, 34.2 mmol) was treated with KF (9.9 g, 170.8 mol) in TG (180.0 mL) at 200 °C for 5 h, followed by isolation as per the above procedure to afford 1*H*,1*H*-perfluoroheptane as a colorless liquid (9.6 g, 23.9 mmol, 70%) [64] [bp: 131–133 °C]. <sup>19</sup>F NMR (CDCl<sub>3</sub>): δ –81.4 (t, *J* = 10 Hz, 3F), –122.6 (m, 4F), –123.3 (m, 4F), –124.2 (m, 2F), –126.6 (m, 2F), –242.2 (tm, *J* = 46 Hz, 1F). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 4.75 (dt, *J* = 46, 12 Hz, 2H).

#### 3.1.4. 1H,1H-Perfluoroctdodecane $(C_{11}F_{23}CH_2F)$

A suspension of 1H,1H-perfluorododecan-1-ol (19.0 g, 31.7 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (50.0 mL), triethylamine (7.68 g, 76.0 mmol) and perfluorobutanesulfonyl fluoride (12.43 g, 41.2 mmol) was stirred for 12 h. After filtration and washing of the residue with water, 1H,1H-perfluorooctylnonaflate was obtained as a white crystalline solid (27.1 g, 30.7 mmol, 97%) [mp: 94–95 °C]. <sup>19</sup>F NMR (Et<sub>2</sub>O):  $\delta$  –81.1 (t, J = 10 Hz, 3F), -81.2 (t, J = 10 Hz, 3F), -110.3 (m, 2F), -119.4 (m, 2F), 121.1 (m, 2F), -121.6 (bs, 12F), -122.5 (m, 4F), -126.1 (m, 4F). <sup>1</sup>H NMR (CCIF<sub>2</sub>CF<sub>2</sub>CI):  $\delta$  4.78 (t, J = 12 Hz, 2H).

1*H*,1*H*-Perfluorododecylnonaflate (20.5 g, 22.9 mmol) was treated with KF (6.63 g, 114.4 mol) in TG (110.0 mL) at 200 °C for 5 h. The resultant solid suspension was dissolved in ether (~300.0 mL) and washed with water (4× 50.0 mL). The ether layer was dried (anhydrous Na<sub>2</sub>SO<sub>4</sub>) and evaporated to obtain 1*H*,1*H*-perfluorododecane as a white crystalline solid (12.0 g, 19.9 mmol, 87%) [mp: 72–73 °C]. <sup>19</sup>F NMR (Et<sub>2</sub>O):  $\delta$  –81.2 (t, *J* = 9 Hz, 3F), -121.7 (m, 10F), -122.1 (m, 2F), -122.7 (m, 2F), -123.0 (m, 2F), -123.7 (m, 2F), -126.3 (m, 2F), -242.6 (tm, *J* = 46 Hz, 1F). <sup>1</sup>H NMR (CClF<sub>2</sub>CF<sub>2</sub>Cl):  $\delta$  4.74 (dt, *J* = 46, 11 Hz, 2H).

# 3.2. Synthesis of the perfluoropropenylzinc reagent [CF<sub>3</sub>CF=CFZnCl] and 1-arylperfluoro-prop-1-enes [CF<sub>3</sub>CF=CFAr]

A 250 mL three-necked RB fitted with a dry ice/isopropanol condenser, septum and a low temperature thermometer were assembled while hot and flushed with nitrogen gas. The flask was charged with ZnCl<sub>2</sub> (3.42 g, 25.0 mmol) and THF (25.0 mL). The solution was cooled to -78 °C and gaseous 1*H*,1*H*-perfluoropropane (2.88 mL, 25.0 mmol) was condensed to the THF solution. A solution of LDA [pre-generated from diisopropylamine (7.7 mL, 55.0 mmol), and *n*-BuLi (22.0 mL, 2.5 M) solution in hexanes, 55.0 mmol in THF (25.0 mL)] in THF was added to this solution slowly (40 min) via a cannula maintaining the temperature of the contents close to -78 °C.

After the addition was completed, the clear yellow reaction mixture was stirred for 30 min and then allowed to warm to RT. The yield of the zinc reagent (mono/bis ~70:30) was 80% and the *E*/*Z* ratio was 89:11. <sup>19</sup>F NMR (THF): [(*E*)-CF<sub>3</sub>CF=CFZnCl]·TMEDA  $\delta$  -69.0 (dd, *J* = 15, 8 Hz, -*CF*<sub>3</sub>), -133.7 (q, *J* = 8 Hz, =*CF*ZnCl), -151.0 (q, *J* = 16 Hz, CF<sub>3</sub>*CF*=). [(*E*)-(CF<sub>3</sub>CF=CF)<sub>2</sub>Zn]·TMEDA  $\delta$  -68.8 (dd, *J* = 16, 9 Hz, -*CF*<sub>3</sub>), -133.2 (q, *J* = 9 Hz, =*CF*ZnCl]. TMEDA/[(*Z*)-(CF<sub>3</sub>CF=CF)<sub>2</sub>Zn]·TMEDA  $\delta$  -69.2 (2 overlapped dd, -*CF*<sub>3</sub>), -147.2 (2 overlapped dq, =*CF*Zn), -177.4 (2 overlapped dq, CF<sub>3</sub>*CF*=).

The THF solution of perfluoropropenylzinc reagent [CF<sub>3</sub>CF=CFZnCl] (10.0 mmol), aryl iodide (6–7 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> were heated at 65 °C in a 250 mL three-necked RB fitted with a reflux condenser, septa and stopper. The reaction mixture was cooled to RT and the products were triturated with either pentane or hexane (4× 20 mL). Careful removal of the solvent under mild vacuum followed by purification of the crude product either by distillation or column chromatography (silica gel) afforded the pure 1-arylperfluoropropenes.

## 3.2.1. (Z)- and (E)-1-phenylperfluoroprop-1-ene $[C_6H_5CF=CFCF_3]$

Following the general procedure for the coupling reaction, THF solution of perfluoropropenylzinc the reagent [CF<sub>3</sub>CF=CFZnCl] (10.3 mmol), iodobenzene (1.34 g, 6.6 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.131 g) were heated at 65 °C for 8 h. The reaction mixture was then cooled to RT and triturated with pentane (4 $\times$  20 mL). The crude product was then chromatographed on silica gel (eluent: pentane) to obtain a mixture of (Z)- and (E)-1-phenylperfluoroprop-1-ene (Z/E87:13) as a colorless liquid in 80% (1.1 g, 5.3 mmol) yield [53]. <sup>19</sup>F NMR (CDCl<sub>3</sub>):  $\delta$  -66.1 (dd, J = 12, 7 Hz, 2.6F, (Z)-CF<sub>3</sub>-), -67.4 (dd, J = 21, 9 Hz, 0.4F, (E)-CF<sub>3</sub>-), -109.5 (quintet, J = 10 Hz, 0.86F, (Z)-Ar-CF=), -146.5 (dq, J = 132, 23 Hz, 0.14F, (*E*)-Ar-*CF*=), -155.0 (dq, *J* = 13, 9 Hz, 0.86F, (*Z*)-R<sub>F</sub>-CF=), -169.9 (dq, J = 131, 11 Hz, 0.14F, (E)-R<sub>F</sub>-CF=). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.68–7.41 (m, 5H, (Z)- and (E)-ArH); GC/ MS: 208 (M<sup>+</sup>, 39), 207 (20), 169 (28), 158 (31), 84 (32), 69 (100, BP). HRMS: calcd. for C<sub>9</sub>H<sub>5</sub>F<sub>5</sub> 208.0311, found 208.0310.

## 3.2.2. (Z)- and (E)-1-(4-fluorophenyl)perfluoroprop-1-ene $[4-FC_6H_4CF=CFCF_3]$

Following the general procedure for the coupling reaction, the perfluoropropenylzinc reagent [CF<sub>3</sub>CF=CFZnCl] (10.3 mmol), 4-fluoroiodobenzene (1.46 g, 6.6 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.131 g) were heated at 65 °C for 8 h. Trituration of the reaction mixture with pentane followed by purification of the crude product by chromatography (eluent: pentane) afforded a mixture of (*Z*)- and (*E*)-1-(4-fluorophenyl)perfluoroprop-1-ene (*Z*/*E* 87:13) as a colorless liquid in 77% (1.15 g, 5.0 mmol) yield. <sup>19</sup>F NMR (CDCl<sub>3</sub>):  $\delta$  –66.2 (dd, *J* = 13, 8 Hz, 2.6F, (*Z*)-*CF*<sub>3</sub>–), –67.6 (dd, *J* = 22, 8 Hz, 0.4F, (*E*)-*CF*<sub>3</sub>–), –110.7 (quintet, *J* = 8 Hz, 0.87F, (*Z*)-Ar-*CF*=), –110.7 (m, 0.87F, (*Z*)-*p*-*F*C<sub>6</sub>H<sub>4</sub>–), –111.5 (m, 0.13F, (*E*)-*p*-*F*C<sub>6</sub>H<sub>4</sub>–), -146.9 (ddq, J = 132, 22, 3 Hz, 0.13F, (*E*)-Ar-*CF*=), -153.3 (dq, J = 13, 7 Hz, 0.87F, (*Z*)-R<sub>F</sub>-*CF*=), -157.7 (dq, J = 132, 9 Hz, 0.13F, (*E*)-R<sub>F</sub>-*CF*=). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.49–7.16 (m, 4H, (*Z*)- and (*E*)-Ar*H*); GC/MS: 226 (*M*<sup>+</sup>, 72), 207 (22), 187 (38), 176 (51), 107 (26), 86 (34), 85 (45), 69 (100, BP); HRMS: calcd. for C<sub>9</sub>H<sub>4</sub>F<sub>6</sub> 226.0217, found 226.0221.

## 3.2.3. (Z)- and (E)-1-(2-methylphenyl)perfluoroprop-1-ene $[2-MeC_6H_4CF=CFCF_3]$

Following the general procedure for the coupling reaction, the perfluoropropenylzinc reagent [CF<sub>3</sub>CF=CFZnCl] (10.0 mmol), 2-iodotoluene (1.42 g, 6.5 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.128 g) were heated at 65 °C for 10 h. Trituration of the reaction mixture with hexane followed by purification of the crude product chromatography (eluent: hexane) afforded a mixture of (Z)- and (E)-1-(2-methylphenyl)perfluoroprop-1ene (Z/E 89:11) as a colorless liquid in 87% (1.25 g, 5.6 mmol) yield. <sup>19</sup>F NMR (CDCl<sub>3</sub>):  $\delta$  -66.0 (dd, J = 10.6, 8 Hz, 2.66F, (Z)- $CF_{3-}$ , -67.4 (dd, J = 22, 11 Hz, 0.35F, (E)- $CF_{3-}$ ), -109.6 (quintet, 7 Hz, 0.89F, (Z)-Ar-CF=), -146.1 (dq, J = 132, 22 Hz, 0.11F, (*E*)-Ar-CF=), -154.4 (dqq, J = 13, 10, 3 Hz,  $0.89F, (Z)-R_F-CF=$ , -169.1 (dqm, J = 132, 11 Hz, 0.11F, (E)- $R_{\rm F}$ -*CF*=). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.42–7.23 (m, 4H, (Z)- and (E)-ArH), 2.37 (d, J = 3 Hz, 3H, (Z)- and (E)-CH<sub>3</sub>): GC/MS: 222 (*M*<sup>+</sup>, 53), 153 (32), 151 (30), 133 (100, BP), 69 (23); HRMS: calcd. for C<sub>10</sub>H<sub>7</sub>F<sub>5</sub> 222.0468, found 222.0471.

#### 3.2.4. (Z)- and (E)-1-(3-methoxyphenyl)perfluoroprop-1ene $[3-MeOC_6H_4CF=CFCF_3]$

Following the general procedure for the coupling reaction, perfluoropropenylzinc reagent [CF<sub>3</sub>CF=CFZnCl] the (10.0 mmol), 3-iodoanisole (1.52 g, 6.5 mmol) and  $Pd(PPh_3)_4$ (0.128 g) were heated at 65 °C for 6 h. Trituration of the reaction mixture with hexane followed by purification of the crude product by chromatography (eluent: 5% CH<sub>2</sub>Cl<sub>2</sub>-hexane) afforded a mixture of (Z)- and (E)-1-(3-methoxyphenyl)perfluoroprop-1-ene (Z/E 90:10) as a colorless liquid in 78% (1.21 g, 5.08 mmol) yield. <sup>19</sup>F NMR (CDCl<sub>3</sub>):  $\delta$  -67.0 (dd, J = 13.1, 8 Hz, 2.7F, (Z)-CF<sub>3</sub>-), -67.8 (dd, J = 22, 12 Hz, 0.3F, (E)- $CF_{3}$ -), -106.2 (m, 0.9F, (Z)-Ar-CF=), -128.8 (dq, J = 141, 21 Hz, 0.1F, (E)-Ar-CF=), -155.3 (quintet, J = 13 Hz, 0.9F, (Z)-R<sub>F</sub>-CF=), -168.6 (dq, J = 141, 10 Hz,  $0.1F, (E)-R_{F}-CF=$ ). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.37–6.98 (m, 4H, (Z)and (E)-ArH), 3.82 (s, 0.3H, (E)-OCH<sub>3</sub>), 3.81 (s, 2.7H, (Z)-OCH<sub>3</sub>); GC/MS: 239 (*M*<sup>+</sup> + 1, 47), 238 (*M*<sup>+</sup>, BP, 100), 219 (37), 208 (55), 207 (41), 187 (45), 175 (50), 169 (37), 158 (65), 145 (89), 139 (43), 125 (58), 119 (43), 125 (58), 119 (43), 69 (40); HRMS: calcd. for C<sub>10</sub>H<sub>7</sub>F<sub>5</sub>O 238.0417, found 238.0417.

#### 3.2.5. (Z)- and (E)-1-(3-

### trifluoromethylphenyl) perfluoroprop-1-ene

 $[3-F_3CC_6H_4CF=CFCF_3]$ 

Following the general procedure for the coupling reaction, the perfluoropropenylzinc reagent [CF<sub>3</sub>CF=CFZnCl] (10.0 mmol), 3-iodobenzotrifluoride (1.76 g, 6.5 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.129 g) were heated at 65 °C for 8 h. Trituration of the reaction mixture with hexane followed by purification of the crude product by chromatography (eluent: hexane) afforded a mixture of (*Z*)- and (*E*)-1-(3-trifluoromethylphenyl)perfluoroprop-1-ene (*Z*/*E* 88:12) as a colorless liquid in 82% (1.47 g, 5.33 mmol) yield. <sup>19</sup>F NMR (CDCl<sub>3</sub>):  $\delta$  –63.6 (s, 3F, (*Z*)- and (*E*)-Ar-*CF*<sub>3</sub>–), -66.2 (dd, *J* = 13, 8 Hz, 2.6F, (*Z*)-*CF*<sub>3</sub>–), -67.6 (dd, *J* = 22, 10 Hz, 0.4F, (*E*)-*CF*<sub>3</sub>–), -111.2 (quintet, 8 Hz, 0.86F, (*Z*)-Ar-*CF*=), -147.3 (dq, *J* = 132, 22 Hz, 0.14F, (*E*)-Ar-*CF*=), -152.5 (dq, *J* = 13, 8 Hz, 0.86F, (*Z*)-R<sub>F</sub>-*CF*=), -167.5 (dq, *J* = 132, 11 Hz, 0.14F, (*E*)-R<sub>F</sub>-*CF*=). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.95–7.58 (m, 4H, (*Z*)- and (*E*)-ArH); GC/MS: 276 (*M*<sup>+</sup>, 37), 226 (34), 207 (46), 187 (39), 138 (21), 86 (44), 84 (67), 69 (100, BP); HRMS: calcd. for C<sub>10</sub>H<sub>4</sub>F<sub>8</sub> 276.0185, found 276.0177.

# 3.3. Synthesis of the perfluorobutenylzinc reagent $[C_2F_5CF=CFZnCl]$ and synthesis of 1-arylperfluoro-1-butenes $[C_2F_5CF=CFAr]$

A 250 mL three-necked RB fitted with a dry ice/isopropanol condenser, septum and a low temperature thermometer was assembled while hot and flushed with nitrogen gas. The flask was charged with ZnCl<sub>2</sub> (1.70 g, 12.5 mmol) and THF (15.0 mL). The solution was cooled to  $-78^{\circ}$ C and gaseous 1H.1H-perfluorobutane (2.53 mL, 12.5 mmol) was condensed to the THF solution. LDA [pre-generated from diisopropylamine (3.85 mL, 27.5 mmol), and n-BuLi (11.0 mL) 2.5 M solution in hexanes, 27.5 mmol in THF (15 mL)] was added to this solution slowly ( $\sim$ 30 min) through a cannula maintaining the temperature of the contents at -78 °C. The clear golden yellow reaction mixture was then stirred -78 °C for an additional 30 min and allowed to warm to RT. The yield of the zinc reagent (monolbis  $\sim$ 65:35) was 76% and the E/Z ratio was 94:6. <sup>19</sup>F NMR (THF):  $[(E)-C_2F_5CF=CFZnC1]$ ·TMEDA  $\delta$ -84.3 (m,  $-CF_3$ ), -118.7 (d, J = 20.5 Hz,  $-CF_2$ ), -128.7 (bs, =CFZnCl), -147.8 (m,  $CF_3CF$ =) [((E)- $CF_3CF$ =CF)<sub>2</sub>Zn]· TMEDA  $\delta$  -84.1 (m, -*CF*<sub>3</sub>), -119.2 (d, *J* = 21.4 Hz, -*CF*<sub>2</sub>), -129.1 (bs, =*CF*Zn), -149.3 (m, *CF*<sub>3</sub>*CF*=).

## 3.3.1. (Z)- and (E)-1-phenylperfluorobut-1-ene $[C_6H_5CF=CFC_2F_5]$

The perfluorobutenylzinc reagent solution  $[C_2F_5CF]$ =CFZnCl] (8.94 mmol), iodobenzene (1.1 g, 5.4 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.107 g) were heated at 65 °C for 6 h. Trituration of the reaction mixture with hexane followed by purification of the crude product by chromatography (eluent: hexane) afforded a mixture of (Z)- and (E)-1-phenylperfluorobut-1-ene (Z/E 93:7) as a colorless liquid in 89% (1.24 g, 4.80 mmol) yield. <sup>19</sup>F NMR (CDCl<sub>3</sub>):  $\delta$  -84.0 (dt, J = 5, 2 Hz, 2.76F, (Z)-CF<sub>3</sub>-),  $-85.0 \text{ (m, } 0.24\text{F, } (E)\text{-}CF_{3}\text{-}), -101.5 \text{ (d, } J = 10 \text{ Hz}, 0.92\text{F, } (Z)\text{-}$ Ar-CF=), -117.1 (d, J = 17 Hz, 1.84F, (Z)- $CF_2$ ), -120.0 (ddq, J = 27, 11.4, 3 Hz, 0.16 F, (*E*)-*CF*<sub>2</sub>-), -145.1 (dtq, J = 132, 26,6 Hz, 0.08F, (E)-Ar-CF=), -153.5 (m, 0.92F, (Z)-R<sub>F</sub>-CF=), -168.5 (dm, J = 132 Hz, 0.08F, (E)-R<sub>F</sub>-CF=). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.54–7.40 (m, 5H, (Z)- and (E)-ArH); GC/MS: 258 (M<sup>+</sup>, 41), 189 (60), 169 (100, BP), 69 (38); HRMS: calcd. for C<sub>10</sub>H<sub>5</sub>F<sub>7</sub> 258.0279, found 258.0276.

### 3.3.2. (Z)- and (E)-1-(4-fluorophenyl)perfluorobut-1-ene $[p-FC_6H_4CF=CFC_2F_5]$

The perfluorobutenylzinc reagent  $[C_2F_5CF=CFZnCl]$ (9.57 mmol), 4-fluoroiodobenzene (1.38 g, 6.2 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.123 g) were heated at 65 °C for 5 h. Trituration of the reaction mixture with hexane followed by purification of the crude product by chromatography (eluent: hexane) afforded a mixture of (Z)- and (E)-1-(4-fluorophenyl)perfluorobut-1-ene (Z/E 94:6) as a colorless liquid in 81% (1.39 g, 5.03 mmol) yield. <sup>19</sup>F NMR (CDCl<sub>3</sub>):  $\delta$  -84.0 (dt, J = 6, 4 Hz, 2.78F, (Z)- $CF_{3-}$ , -85.0 (m, 0.23F, (E)- $CF_{3-}$ ), -100.9 (dt, J = 11, 6 Hz, 0.93F, (Z)-Ar-CF=), -107.3 (m, 0.06F, (E)-Ar-F), -107.4 (m, 0.94F, (Z)-Ar-F), -117.0 (d, J = 17 Hz, 1.86F, (Z)-CF<sub>2</sub>-),  $-120.0 (ddq, J = 27, 12, 2 Hz, 0.14 F, (E)-CF_{2}), -144.7 (dtq, J = 27, 12, 2 Hz, 0.14 F, (E)-CF_{2}), -144.7 (dtq, J = 27, 12, 2 Hz, 0.14 F, (E)-CF_{2}), -144.7 (dtq, J = 27, 12, 2 Hz, 0.14 F, (E)-CF_{2}), -144.7 (dtq, J = 27, 12, 2 Hz, 0.14 F, (E)-CF_{2}), -144.7 (dtq, J = 27, 12, 2 Hz, 0.14 F, (E)-CF_{2}), -144.7 (dtq, J = 27, 12, 2 Hz, 0.14 F, (E)-CF_{2}), -144.7 (dtq, J = 27, 12, 2 Hz, 0.14 F, (E)-CF_{2}), -144.7 (dtq, J = 27, 12, 2 Hz, 0.14 F, (E)-CF_{2}), -144.7 (dtq, J = 27, 12, 2 Hz, 0.14 F, (E)-CF_{2}), -144.7 (dtq, J = 27, 12, 2 Hz, 0.14 F, (E)-CF_{2}), -144.7 (dtq, J = 27, 12, 2 Hz, 0.14 F, (E)-CF_{2})), -144.7 (dtq, J = 27, 12, 2 Hz, 0.14 F, (E)-CF_{2})), -144.7 (dtq, J = 27, 12, 2 Hz, 0.14 F, (E)-CF_{2})), -144.7 (dtq, J = 27, 12, 2 Hz, 0.14 F, (E)-CF_{2})), -144.7 (dtq, J = 27, 12, 2 Hz, 0.14 F, (E)-CF_{2})), -144.7 (dtq, J = 27, 12, 2 Hz, 0.14 F, (E)-CF_{2})), -144.7 (dtq, J = 27, 12, 2 Hz, 0.14 F, (E)-CF_{2})))$ J = 133, 27, 6 Hz, 0.07F, (E)-Ar-CF=), -152.5 (m, 0.93F, (Z)- $R_{F}-CF=$ ), -168.7 (dm, J = 132 Hz, 0.07F, (E)- $R_{F}-CF=$ ). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.45 (m, 2H, (Z)- and (E)-ArH), 7.14 (m, 2H, (Z)- and (E)-ArH); GC/MS: 276 (M<sup>+</sup>, 30), 207 (66), 187 (BP, 100), 86 (47), 84 (70), 69 (74), 51 (51); HRMS: calcd. for C<sub>10</sub>H<sub>4</sub>F<sub>8</sub> 276.0185, found 276.0190.

#### 3.3.3. (Z)- and (E)-1-(2-isopropylphenyl)perfluorobut-1ene $[2-(CH_3)_2CHC_6H_4CF=CFC_2F_5]$

The perfluorobutenylzinc reagent solution  $[C_2F_5CF=C]$ FZnCl] (8.0 mmol), 2-isopropyliodobenzene (1.22 g, 5.0 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.100 g) were heated at 65 °C for 18 h. Trituration of the reaction mixture with hexane followed by purification of the crude product by chromatography (eluent: hexane) afforded a mixture of (Z)- and (E)-1-(2-isopropylphenyl)perfluorobut-1-ene (Z/E 94:6) as a colorless liquid in 71% (1.05 g, 3.5 mmol) yield. <sup>19</sup>F NMR (CDCl<sub>3</sub>):  $\delta$  -84.1 (dt, J = 7,  $3.0 \text{ Hz}, 2.8F, (Z)-CF_3-$ ,  $-85.1 \text{ (m, } 0.18F, (E)-CF_3), -95.6 \text{ (d,}$ J = 14 Hz, 0.94F, (Z)-Ar-CF=), -117.6 (d, J = 17 Hz, 1.88F, (Z)- $CF_{2}$ -), -120.5 (ddq, J = 25, 13, 2 Hz, 0.12F, (E)- $CF_{2}$ -), -122.0 (dtm, J = 143, 26 Hz, 0.06F, (E)-Ar-CF=), -153.2 (m,0.94F, (Z)-R<sub>F</sub>-CF=), -166.0 (dm, J = 143 Hz, 0.06F, (E)-R<sub>F</sub>-CF=). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.52–7.19 (m, 4H, (Z)- and (E)-ArH), 3.03 (m, 0.94H, (Z)-(CH<sub>3</sub>)<sub>2</sub>CH-), 2.63 (m, 0.06H, (E)- $(CH_3)_2CH_{-}$ , 1.26 (d, J = 7 Hz, 0.35H,  $(E)_{-}(CH_3)_{2-}$ ), 1.25 (d, J = 7 Hz, 0.5.65H, (Z)-(CH<sub>3</sub>)<sub>2</sub>-); GC/MS: 300 ( $M^+$ , 75), 285 (BP, 100), 267 (20), 245 (36), 166 (26), 151 (46), 146 (84), 133 (33), 129 (44), 115 (23), 69 (94); HRMS: calcd. for C<sub>9</sub>H<sub>4</sub>F<sub>5</sub> 300.0749, found 300.0750.

### 3.3.4. (Z)- and (E)-1-(3-

### trifluoromethylphenyl)perfluorobut-1-ene [3- $F_3CC_6H_4CF=CFC_2F_5$ ]

The perfluorobutenylzinc reagent solution [C<sub>2</sub>F<sub>5</sub>CF=C FZnCl] (8.0 mmol), 3-iodobenzotrifluoride (1.35 g, 5.0 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.100 g) were heated at 65 °C for 8 h. Trituration of the reaction mixture with hexane followed by purification of the crude product by chromatography (eluent: hexane) afforded a mixture of (*Z*)- and (*E*)-1-(3-trifluoromethylphenyl)perfluorobut-1-ene (*Z*/*E* 93:7) as a colorless liquid in 78% (1.20 g, 4.1 mmol) yield. <sup>19</sup>F NMR (CDCl<sub>3</sub>):  $\delta$  -63.6 (s, 2.75F, (*Z*)-ArCF<sub>3</sub>), -63.7 (s, 0.25F, (*E*)-ArCF<sub>3</sub>), -84.0 (dt, *J* = 4, 2 Hz, 2.75F, (*Z*)-CF<sub>3</sub>-), -85.0 (m, 0.26F, (*E*)-

 $CF_{3-}$ ), -103.3 (bd, J = 10 Hz, 0.92F, (Z)-Ar-CF=), -117.2 (d, J = 16 Hz, 1.84F, (Z)- $CF_{2-}$ ), -120.2 (dd, J = 26, 12 Hz, 0.16F, (E)- $CF_{2-}$ ), -145.8 (dtq, J = 133, 28, 6 Hz, 0.08F, (E)-Ar-CF=), -151.0 (m, 0.92F, (Z)-R<sub>F</sub>-CF=), -168.7 (dm, J = 134 Hz, 0.08F, (E)-R<sub>F</sub>-CF=). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.92–7.58 (m, 4H, (Z)- and (E)-ArH); GC/MS: 326 ( $M^{+}$ , 64), 307 (20), 257 (100, BP), 237 (82), 188 (25), 187 (41), 169 (32), 69 (34); HRMS: calcd. for C<sub>11</sub>H<sub>4</sub>F<sub>10</sub> 326.0153, found 326.0154.

# 3.4. Synthesis of the perfluorohexenylzinc reagent [C<sub>4</sub>F<sub>9</sub>CF=CFZnCl] and synthesis of 1-arylperfluoro-1-hexene [n-C<sub>4</sub>F<sub>9</sub>CF=CFAr]

Following the standard procedure for the preparation of perfluoroalkenylzinc reagents, metallation of 1*H*,1*H*-perfluorohexane (2.82 g, 9.3 mmol) with LDA (20.5 mmol) in presence of ZnCl<sub>2</sub> (1.27 g, 9.3 mmol) afforded the perfluorohexenylzinc reagent (*mono/bis* ~70:30) as a dark-brown solution in 75% yield with *E/Z* ratio 96:4. <sup>19</sup>F NMR (THF): [(*E*)-C<sub>4</sub>F<sub>9</sub>CF=CFZnCl]·TMEDA  $\delta$  -81.5 (t, *J* = 10 Hz, -*CF*<sub>3</sub>), -115.4 (m, =CF*CF*<sub>2</sub>), -123.3 (m, -*CF*<sub>2</sub>), -123.3 (m, -*CF*<sub>2</sub>), -126.1 (s, =*CF*ZnCl), -126.7 (m, *CF*<sub>2</sub>), -152.1 (m, CF<sub>2</sub>*CF*=) [((*E*)-C<sub>4</sub>F<sub>9</sub>CF=CF)<sub>2</sub>Zn]·TMEDA  $\delta$  -81.6 (t, *J* = 10 Hz, -*CF*<sub>3</sub>), -114.8 (m, =CF*CF*<sub>2</sub>), -122.4 (m, =*CF*<sub>2</sub>), -123.0 (m, -*CF*<sub>2</sub>), -125.5 (s, =*CF*Zn), -126.5 (m, *CF*<sub>2</sub>), -151.2 (m, CF<sub>2</sub>*CF*=).

# 3.4.1. (Z)- and (E)-1-phenylperfluorohex-1-ene $[C_6H_5CF=CFC_4F_9]$

The perfluorohexenylzinc reagent solution  $[C_4F_9CF=C]$ FZnCl] (1.5 mmol), iodobenzene (0.204 g, 1.0 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.025 g) were heated at 65 °C for 8 h. Trituration of the reaction mixture with hexane followed by purification of the crude product by chromatography over silica gel (eluent: hexane) afforded a mixture of (Z)- and (E)-1-phenylperfluorohex-1-ene (Z/E 96:4) as a colorless liquid in 81% (0.291 g, 0.81 mmol) yield [42]. <sup>19</sup>F NMR (CDCl<sub>3</sub>):  $\delta$  -81.4 (t, J = 10 Hz, 3F, (Z)- and (E)-CF<sub>3</sub>-), -99.9 (d, J = 10 Hz, 0.96F, (Z)-Ar-CF=), -113.9 (q, J = 14 Hz, 1.92F, (Z)- $CF_2$ ), -117.1 (m, 0.08F, (*E*)-*CF*<sub>2</sub>-), -123.4 (m, 1.92F, (*Z*)-*CF*<sub>2</sub>-), -125.0 (m, 0.08F, (E)-CF<sub>2</sub>-), -126.8 (m, 1.92F, (Z)-CF<sub>2</sub>-), -126.9 (m, 0.08F, (*E*)-*CF*<sub>2</sub>-), -144.6 (dm, J = 132 Hz, 0.04F, (E)-Ar-CF=), -152.3 (m, 0.96F, (Z)-R<sub>F</sub>-CF=), -167.3 (dm, J = 132 Hz, 0.04F, (E)-R<sub>F</sub>-CF=). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.56– 7.40 (m, 5H, (Z)- and (E)-ArH); GC/MS: 358 ( $M^+$ , 5), 189 (59), 169 (100, BP), 69 (34); HRMS: calcd. for C<sub>12</sub>H<sub>5</sub>F<sub>11</sub> 358.0216, found 358.0222.

## 3.4.2. (Z)- and (E)-1-(2-methylphenyl)perfluorohex-1-ene $[2-MeC_6H_4CF=CFC_4F_9]$

The perfluorohexenylzinc reagent solution  $[C_4F_9CF=C$  FZnCl] (1.5 mmol), 2-iodotoulene (0.218 g, 1.0 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.025 g) were heated at 65 °C for 15 h. Trituration of the reaction mixture with hexane followed by purification of the crude product by chromatography (eluent: hexane) afforded a mixture of (*Z*)- and (*E*)-1-(2-methylphenyl)perfluorohex-1-ene (*Z*/*E* 96:4) as a colorless liquid in 81% (0.302 g, 0.81 mmol) yield. <sup>19</sup>F NMR (CDCl<sub>3</sub>):  $\delta$  –81.4 (t, *J* = 10 Hz, 3F, (*Z*)- and (*E*)-

*CF*<sub>3</sub>−), −99.0 (d, *J* = 13 Hz, 0.95F, (*Z*)-Ar-*CF*=), −114.6 (q, *J* = 13 Hz, 1.9F, (*Z*)-*CF*<sub>2</sub>−), −117.4 (m, 0.1F, (*E*)-*CF*<sub>2</sub>−), −123.7 (m, 1.9F, (*Z*)-*CF*<sub>2</sub>−), −125.0 (m, 0.1F, (*E*)-*CF*<sub>2</sub>−), −126.8 (m, 1.9F, (*Z*)-*CF*<sub>2</sub>−), −126.8 (m, 0.1F, (*E*)-*CF*<sub>2</sub>−), −144.5 (dm, not resolved, 0.05F, (*E*)-Ar-*CF*=), −152.3 (m, 0.95F, (*Z*)-R<sub>F</sub>-*CF*=), −165.4 (dm, *J* = 142 Hz, 0.05F, (*E*)-R<sub>F</sub>-*CF*=). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.45–7.20 (m, 4H, (*Z*)- and (*E*)-Ar*H*), 2.37 (d, *J* = 2.7 Hz, 3H, (*Z*)- and (*E*)-*CH*<sub>3</sub>); GC/MS: 372 (*M*<sup>+</sup>, 67), 183 (100, BP), 169 (24), 153 (31), 151 (56), 134 (43), 133 (83), 69 (40); HRMS: calcd. for C<sub>13</sub>H<sub>7</sub>F<sub>11</sub> 372.0372, found 372.0371.

### 3.4.3. (Z)- and (E)-1-(4-methoxyphenyl)perfluorohex-1-ene $[4-MeOC_6H_4CF=CFC_4F_9]$

The perfluorohexenylzinc reagent solution  $[C_4F_9CF=C]$ FZnCl] (1.5 mmol), 4-iodoanisole (0.234 g, 1.0 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.025 g) were heated at 65 °C for 6 h. Trituration of the reaction mixture with hexane followed by purification of the crude product by chromatography (eluent: 5% CH<sub>2</sub>Cl<sub>2</sub>-hexane) produced a mixture of (Z)- and (E)-1-(4-methoxyphenyl)perfluorohex-1-ene (Z/E 96:4) as a colorless liquid in 79% (0.306 g, 0.79 mmol) yield. <sup>19</sup>F NMR (CDCl<sub>3</sub>):  $\delta$  -81.4 (t, J = 9 Hz, 3F, (Z)- and (E)-CF<sub>3</sub>-), -98.4 (d, J = 12 Hz, 0.95F, (Z)-Ar-CF=), -113.7 (q, J = 15 Hz, 1.9F, (Z)- $CF_2-$ ), -116.8  $(m, 0.1F, (E)-CF_{2}), -123.4 (m, 1.9F, (Z)-CF_{2}), -125.0 (m,$  $0.1F, (E)-CF_{2}$ ,  $-126.8 (m, 1.9F, (Z)-CF_{2}), -126.9 (m, 0.1F, (Z)-CF_{2})$ (E)- $CF_{2}$ -), -144.5 (dm, J = 131 Hz, 0.05F, (E)-Ar-CF=), -153.0 (m, 0.95F, (Z)-R<sub>F</sub>-CF=), -170.0 (dm, J = 131 Hz, 0.05F, (*E*)- $R_{F}$ -*CF*=). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.65 (d, *J* = 9 Hz, 0.10H, (E)-ArH), 7.37 (d, J = 8 Hz, 1.8H, (Z)-ArH), 7.00 (d, *J* = 9 Hz, 0.10H, (*E*)-Ar*H*), 6.93 (d, *J* = 9 Hz, 1.8H, (*Z*)-Ar*H*), 3.86 (s, 0.15H, (E)-Ar-OCH<sub>3</sub>), 3.85 (2.85H, (E)-Ar-OCH<sub>3</sub>); GC/MS: 388 (M<sup>+</sup>, 41), 369 (15), 219 (BP, 100), 199 (59), 169 (22), 69 (24); HRMS: calcd. for C<sub>13</sub>H<sub>7</sub>F<sub>11</sub>O 388.0321, found 388.0315.

#### *3.4.4.* (*Z*)- and (*E*)-1-(*3*trifluoromethylphenyl)perfluorohex-1-ene

### $[3-CF_3C_6H_5CF=CFC_4F_9]$

The perfluorohexenylzinc reagent solution  $[C_4F_9CF=C]$ FZnCl] (1.5 mmol), 3-iodobenzotrifluoride (0.272 g, 1.0 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.025 g) were heated at 65  $^{\circ}$ C for 8 h. Trituration of the reaction mixture with hexane followed by purification of the crude product by chromatography (eluent: hexane) produced a mixture of (Z)- and (E)-1-(3-trifluoromethylphenyl)perfluorohex-1-ene (Z/E 95:5) as a colorless liquid in 78% (0.332 g, 0.78 mmol) yield. <sup>19</sup>F NMR (CDCl<sub>3</sub>):  $\delta$ -63.61 (s, 0.15F, (E)-ArCF<sub>3</sub>), -63.65 (s, 2.85F, (Z)-ArCF<sub>3</sub>), -81.4 (m, 3F, (Z)- and (E)-CF<sub>3</sub>-), -101.9 (bs, 0.95F, (Z)-Ar-CF=), -114.1 (m, 1.92F, (Z)- $CF_2$ -), -117.3 (m, 0.1F, (E)- $CF_{2}$ -), -123.4 (m, 1.9F, (Z)- $CF_{2}$ -), -124.9 (m, 0.1F, (E)- $CF_{2}$ -), -126.8 (m, 1.9F, (Z)- $CF_{2}$ -), -126.8 (m, 0.1F, (E)- $CF_{2}$ -), -144.5 (dm, J = 132 Hz, 0.05F, (E)-Ar-CF=), -149.7 (m, 0.95F, (Z)- $R_F$ -CF=), -169.7 (dm, J = 132 Hz, 0.05F, (E)- $R_{F}-CF=$ ). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.97–7.44 (m, 4H, (Z)- and (E)-ArH); GC/MS: 426 (M<sup>+</sup>, 40), 407 (28), 257 (BP, 100), 237 (92), 188 (55), 187 (72), 169 (73), 69 (59). HRMS: calcd. for C<sub>13</sub>H<sub>4</sub>F<sub>14</sub> 426.0089, found 426.0087.

3.5. Synthesis of the perfluoroheptenylzinc reagent  $[C_5F_{11}CF=CFZnCl]$  and synthesis of 1-arylperfluoro-1-heptene  $[n-C_5F_{11}CF=CFAr]$ 

Following the standard procedure for the preparation of perfluoroalkenylzinc reagent, metallation of 1*H*,1*H*-perfluoroheptane (3.54 g, 10.1 mmol) with LDA (22.2 mmol) in presence of ZnCl<sub>2</sub> (1.39 g, 10.1 mmol) and obtained the zinc reagent (*mono/bis* ~60:40) as a pink-brown solution in 83% yield with *E/* Z ratio 99:1. <sup>19</sup>F NMR (THF): [(*E*)-C<sub>5</sub>F<sub>11</sub>CF=CFZnCl]·TMEDA  $\delta$  -81.5 (t, *J* = 9 Hz, -*CF*<sub>3</sub>), -114.8 (m, -*CF*<sub>2</sub>), -122.6 (m, -*CF*<sub>2</sub>), -123.3 (m, -*CF*<sub>2</sub>), -126.6 (m, *CF*<sub>2</sub>), -127.8 (s, =*CF*ZnCl), -146.5 (m, CF<sub>2</sub>*CF*=); [((*E*)-C<sub>5</sub>F<sub>11</sub>CF=CF)<sub>2</sub> Zn]·TMEDA  $\delta$  -81.6 (t, *J* = 10 Hz, -*CF*<sub>3</sub>), -115.5 (m, -*CF*<sub>2</sub>), -122.3 (m, -*CF*<sub>2</sub>), -123.0 (m, -*CF*<sub>2</sub>), -126.6 (m, *CF*<sub>2</sub>), -127.4 (s, =*CF*Zn), -148.3 (m, CF<sub>2</sub>*CF*=).

## 3.5.1. (Z)-1-Phenylperfluorohept-1-ene $[C_6H_5CF=CFC_5F_{11}]$

The perfluoroheptenylzinc reagent solution  $[C_5F_{11}$ CF=CFZnCl] (1.7 mmol), iodobenzene (0.204 g, 1.0 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.025 g) were heated at 65 °C for 8 h. Trituration of the reaction mixture with hexane followed by purification of the crude product by chromatography (eluent: hexane) afforded pure (*Z*)-1-phenylperfluorohept-1-ene as a colorless liquid in 89% (0.363 g, 0.89 mmol) yield. <sup>19</sup>F NMR (CDCl<sub>3</sub>):  $\delta$  -81.3 (t, *J* = 10 Hz, 3F, *CF*<sub>3</sub>-), -99.9 (d, *J* = 10 Hz, 1F, Ar-*CF*=), -113.7 (q, *J* = 12 Hz, 2F, *CF*<sub>2</sub>-), -122.7 (m, 2F, *CF*<sub>2</sub>-), -123.4 (m, 2F, *CF*<sub>2</sub>-), -126.7 (m, 2F, *CF*<sub>2</sub>-), -152.2 (m, 1F, R<sub>F</sub>-*CF*=). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.45-7.20 (m, 5H, Ar*H*); GC/MS: 408 (*M*<sup>+</sup>, 31), 189 (73), 169 (100, BP), 69 (62); HRMS: calcd. for C<sub>13</sub>H<sub>5</sub>F<sub>13</sub> 408.0184, found 408.0186.

# 3.5.2. (Z)-1-(4-Fluorophenyl)perfluorohept-1-ene [4- $FC_6H_4CF=CFC_5F_{11}$ ]

The perfluoroheptenylzinc reagent solution  $[C_5F_{11}CF=C]$ FZnCl] (1.7 mmol), 4-fluoroiodobenzene (0.222)g, 1.0 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.025 g) were heated at 65  $^{\circ}$ C for 12 h. Trituration of the reaction mixture with hexane followed by purification of the crude product by chromatography (eluent: hexane) afforded pure (Z)-1-(4-fluorophenyl)perfluorohept-1-ene as a colorless liquid in 91% (0.390 g, 0.91 mmol) yield. <sup>19</sup>F NMR (CDCl<sub>3</sub>):  $\delta$  -81.3 (t, J = 11 Hz, 3F, CF<sub>3</sub>-), -99.9 (dm, not resolved, 1F, Ar-CF=), -107.4 (m, 1F, ArF-), -113.7 (q, J = 13 Hz, 2F,  $CF_2$ -), -122.7 (m, 2F, CF<sub>2</sub>-), -123.4 (m, 2F, CF<sub>2</sub>-), -126.7 (m, 2F, CF<sub>2</sub>-), -151.2 (m, 1F, R<sub>F</sub>-CF=). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.47 (t, distorted, 2H), 7.14 (tm, J = 8 Hz, 2H); GC/MS: 426 ( $M^+$ , 48), 407 (14), 207 (100, BP), 187 (91), 169 (36), 138 (34), 119 (32), 69 (78). HRMS: calcd. for C<sub>13</sub>H<sub>4</sub>F<sub>14</sub> 426.0089, found 426.0099.

## 3.5.3. (Z)-1-(3-Trifluoromethylphenyl)perfluoro-1-heptene $[3-CF_3C_6H_4CF=CFC_5F_{11}]$

The perfluoroheptenylzinc reagent solution  $[C_5F_{11}]$  CF=CFZnCl] (1.7 mmol), 3-iodobenzotrifluoride (0.234 g,

1.0 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.025 g) were heated at 65 °C for 12 h, Trituration of the reaction mixture with hexane followed by purification of the crude product by chromatography (eluent: hexane) afforded pure (*Z*)-1-(3-trifluoromethylphenyl)perfluorohept-1-ene as a colorless liquid in 86% (0.408 g, 0.86 mmol) yield. <sup>19</sup>F NMR (CDCl<sub>3</sub>):  $\delta$  –63.7 (s, 3F, Ar-*CF*<sub>3</sub>), -81.4 (t, *J* = 10 Hz, 3F, *CF*<sub>3</sub>-), -101.9 (d, *J* = 7.0 Hz, 1F, Ar-*CF*=), -113.9 (q, *J* = 12 Hz, 2F, *CF*<sub>2</sub>-), -122.6 (m, 2F, *CF*<sub>2</sub>-), -123.3 (m, 2F, *CF*<sub>2</sub>-), -126.7 (m, 2F, *CF*<sub>2</sub>-), -149.7 (m, 1F, R<sub>F</sub>-*CF*=). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.80 (d, *J* = 8 Hz, 1H), 7.73 (s, 1H), 7.67-7.57 (m, 2H); GC/MS: 476 (*M*<sup>+</sup>, 58), 457 (48), 258 (36), 257 (100, BP), 237 (84), 188 (57), 187 (67), 169 (72), 119 (31), 69 (77); HRMS: calcd. for C<sub>14</sub>H<sub>4</sub>F<sub>16</sub> 476.0058, found 476.0061.

### 3.5.4. (Z)-1-(4-Methoxyphenyl)perfluorohept-1-ene [4- $MeOC_6H_4CF=CFC_5F_{11}$ ]

The perfluoroheptenylzinc reagent solution  $[C_5F_{11}CF=C$  FZnCl] (1.7 mmol), 4-iodoanisole (0.234 g, 1.0 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.025 g) were heated at 65 °C for 8 h. Trituration of the reaction mixture with hexane followed by purification of the crude product by chromatography (eluent: 5% CH<sub>2</sub>Cl<sub>2</sub>-hexane) afforded pure (*Z*)-1-(4-methoxyphenyl)perfluorohept-1-ene as a colorless liquid in 92% (0.402 g, 0.92 mmol) yield. <sup>19</sup>F NMR (CDCl<sub>3</sub>):  $\delta$  -81.3 (t, *J* = 10 Hz, 3F, *CF*<sub>3</sub>-), -98.4 (d, *J* = 12 Hz, 1F, Ar-*CF*=), -113.5 (q, *J* = 14 Hz, 2F, *CF*<sub>2</sub>-), -122.6 (m, 2F, *CF*<sub>2</sub>-), -123.3 (m, 2F, *CF*<sub>2</sub>-), -126.7 (m, 2F, *CF*<sub>2</sub>-), -152.9 (m, 2F, R<sub>F</sub>-*CF*=). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.38 (dd, *J* = 8, 1 Hz, 2H), 6.94 (d, *J* = 8 Hz, 2H), 3.84 (s, 3H); GC/MS: 438 (*M*<sup>+</sup>, 31), 189 (73), 169 (100, BP), 69 (62); HRMS: calcd. for C<sub>14</sub>H<sub>7</sub>F<sub>13</sub> 438.0289, found 438.0289.

### 3.5.5. (Z)- and (E)-1-(2-methyl-6nitrophenyl)perfluorohept-1-ene $[2-Me(6-NO_2)C_6H_3CF=CFC_5F_{11}]$

The perfluoroheptenylzinc reagent solution  $[C_5F_{11}CF=C]$ FZnCl] (1.7 mmol), 2-methyl-6-nitroiodobenzene (0.263 g, 1.0 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.025 g) were heated at 65  $^{\circ}$ C for 24 h. Trituration of the reaction mixture with hexane followed by purification of the crude product by chromatography (eluent: hexane) afforded a mixture of (Z)- and the (E)-1-(2-methyl-6nitrophenyl)perfluorohept-1-ene as a colorless liquid in 31% (0.145 g, 0.31 mmol) yield with Z/E ratio 91:9. <sup>19</sup>F NMR  $(CDCl_3): \delta - 81.3 (t, J = 10 Hz, 3F, (Z) - and (E) - CF_3 -), -102.8$ (bd, J = 8 Hz, 0.9F, (Z)-Ar-CF=), -114.6 (q, J = 12 Hz, 1.8F, (Z)- $CF_2$ -), -117.4 (m, 0.18F, (E)- $CF_2$ -), -122.9 (m, 1.8F, (Z)-CF<sub>2</sub>-), -123.2 (m, 0.36F, 2(E)-CF<sub>2</sub>-), -123.3 (m, 1.8F, (Z)- $CF_{2}$ -), -124.1 (m, 0.18F, (E)- $CF_{2}$ -), -126.6 (m, 1.8F, (Z)- $CF_{2}$ -), -129.2 (dm, J = 142 Hz, 0.09F, (E)-Ar-CF=), -149.1 (m, 0.9F, (Z)- $R_F$ -CF=), -162.0 (dm, J = 142 Hz, 0.09F, (E)- $R_{F}-CF=$ ). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  8.09 (s, 1H), 8.02 (d, J = 9 Hz, 1H), 7.44 (d, *J* = 8 Hz, 1H), 2.42 (d, *J* = 2 Hz, 3H); GC/MS:  $467 (M^+, 11), 248 (10), 202 (44), 182 (21), 151 (43), 119 (31),$ 69 (100, BP); HRMS: calcd. for C<sub>14</sub>H<sub>6</sub>NO<sub>2</sub>F<sub>13</sub> 467.0191, found 467.0192.

3.6. Synthesis of the perfluorooctenylzinc reagent  $[C_5F_{11}CF=CFZnCl]$  and synthesis of 1-arylperfluoro-1-octenes  $[n-C_6F_{13}CF=CFAr]$ 

Following the standard procedure for the preparation of perfluoroalkenylzinc reagent, metallation of 1*H*,1*H*-perfluorooctane (6.03 g, 15.0 mmol) with LDA (33.0 mmol) in presence of ZnCl<sub>2</sub> (2.04 g, 15.0 mmol) afforded [C<sub>6</sub>F<sub>13</sub>CF=CFZnCl] as a pink-brown solution in 79% yield with *E*/Z ratio 98:2. <sup>19</sup>F NMR (CDCl<sub>3</sub>): [(*E*)-C<sub>6</sub>F<sub>13</sub>CF=CFZnCl]·TMEDA  $\delta$  -81.5 (t, *J* = 9.9 Hz, -*CF*<sub>3</sub>), -114.4 (m, =CFCF<sub>2</sub>), -122.4 (m, 2*CF*<sub>2</sub>), -123.2 (m, -*CF*<sub>2</sub>), -126.5 (m, *CF*<sub>2</sub>), -127.4 (s, =*CF*ZnCl), -144.6 (m, CF<sub>2</sub>*CF*=).

### 3.6.1. (Z)-1-Phenylperfluorooct-1-ene $[C_6H_5CF=CFC_6F_{13}]$

The perfluorooctenylzinc reagent solution  $[C_6F_{13}CF=C$  FZnCl] (4.06 mmol), iodobenzene (0.579 g, 2.8 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.056 g) were heated at 65 °C for 6 h. Trituration of the reaction mixture with hexane followed by purification of the crude product by chromatography (eluent: hexane) afforded pure (*Z*)-1-phenylperfluorooct-1-ene as a colorless liquid in 81% (1.05 g, 2.3 mmol) yield [42]. <sup>19</sup>F NMR (CDCl<sub>3</sub>):  $\delta$  –81.3 (t, *J* = 9 Hz, 3F, *CF*<sub>3</sub>–), -99.9 (d, *J* = 9 Hz, 1F, Ar-*CF*=), -113.7 (q, *J* = 12 Hz, 2F, *CF*<sub>2</sub>–), -122.5 (m, 4F, 2*CF*<sub>2</sub>–), -123.3 (m, 2F, *CF*<sub>2</sub>–), -126.6 (m, 2F, *CF*<sub>2</sub>), -152.2 (m, 1F, R<sub>F</sub>-*CF*=). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.53–7.44 (m, 5H, Ar*H*); GC/MS: 458 (*M*<sup>+</sup>, 35), 439 (10), 200 (15), 190 (23), 189 (100, BP), 169 (92), 151 (17), 119 (17), 69 (28); HRMS: calcd. for C<sub>14</sub>H<sub>5</sub>F<sub>15</sub> 458.0152, found 458.0156.

## 3.6.2. (Z)-1-(4-Fluorophenyl)perfluorooct-1-ene $[4-FC_6H_4CF=CFC_6F_{13}]$

The perfluorooctenylzinc reagent solution  $[C_6F_{13}CF=C$  FZnCl] (2.7 mmol), 4-fluoroiodobenzene (0.360 g, 1.6 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.030 g) were heated at 65 °C for 15 h. Trituration of the reaction mixture with hexane followed by purification of the crude product by chromatography (eluent: hexane) afforded pure (*Z*)-1-(4-fluorophenyl)perfluorooct-1-ene as a colorless liquid in 91% (0.692 g, 1.5 mmol) yield. <sup>19</sup>F NMR (CDCl<sub>3</sub>):  $\delta$  -81.3 (t, *J* = 10 Hz, 3F, *CF*<sub>3</sub>-), -99.2 (dm, not resolved, 1F, Ar-*CF*=), -107.4 (m, 1F, Ar*F*-), -113.7 (q, *J* = 13 Hz, 2F, *CF*<sub>2</sub>-), -122.5 (m, 4F, 2*CF*<sub>2</sub>-), -123.2 (m, 2F, *CF*<sub>2</sub>-), -126.6 (m, 2F, *CF*<sub>2</sub>-), -151.1 (m, 1F, R<sub>F</sub>-*CF*=). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.45 (dd, *J* = 7, 5 Hz, 2H), 7.14 (tm, *J* = 8 Hz, 2H); GC/MS: 476 (*M*<sup>+</sup>, 35), 457 (13), 207 (100, BP), 187 (88), 169 (23), 69 (38); HRMS: calcd. for C<sub>13</sub>H<sub>4</sub>F<sub>14</sub> 476.0058, found 476.0058.

## 3.6.3. (Z)-1-(3-Trifluoromethylphenyl)perfluorooct-1-ene $[3-CF_3C_6H_4CF=CFC_6F_{13}]$

The perfluorooctenylzinc reagent solution  $[C_6F_{13}CF=C$  FZnCl] (2.7 mmol), 4-iodobenzotrifluoride (0.440 g, 1.6 mmol) and Pd(PPh\_3)\_4 (0.030 g) were heated at 65 °C for 10 h. Trituration with hexane followed by purification of the crude product by chromatography (eluent: hexane) afforded pure (*Z*)-1-(3-trifluoromethylphenyl)perfluorooct-1-ene as a

colorless liquid in 95% (0.795 g, 1.5 mmol) yield. <sup>19</sup>F NMR (CDCl<sub>3</sub>):  $\delta$  -63.7 (s, 3F, Ar-*CF*<sub>3</sub>), -81.3 (t, *J* = 10 Hz, 3F, *CF*<sub>3</sub>-), -101.8 (d, *J* = 7 Hz, 1F, Ar-*CF*=), -113.8 (q, *J* = 13 Hz, 2F, *CF*<sub>2</sub>-), -122.5 (m, 4F, 2*CF*<sub>2</sub>-), -123.3 (m, 2F, *CF*<sub>2</sub>-), -126.6 (m, 2F, *CF*<sub>2</sub>-), -149.6 (m, 1F, R<sub>F</sub>-*CF*=). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.80 (d, *J* = 7 Hz, 1H), 7.73 (s, 1H), 7.64 (t, distorted, 1H), 7.58 (d, *J* = 8 Hz, 1H); GC/MS: 476 (*M*<sup>+</sup>, 30), 507 (20), 257 (50), 237 (59), 187 (25), 169 (32), 119 (35), 69 (100, BP); HRMS: calcd. for C<sub>15</sub>H<sub>4</sub>F<sub>18</sub> 526.0026, found 526.0040.

## 3.6.4. (Z)-1-(4-Methoxyphenyl)perfluoro-1-octene $[4-MeOC_6H_4CF=CFC_6F_{13}]$

The perfluorooctenylzinc reagent solution  $[C_6F_{13}CF=C$  FZnCl] (2.7 mmol), 4-iodoanisol (0.370 g, 1.6 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.030 g) were heated at 65 °C for 8 h. Trituration of the reaction mixture with hexane followed by purification of the crude product by chromatography (eluent: 5% CH<sub>2</sub>Cl<sub>2</sub>–hexane) afforded pure (*Z*)-1-(4-methoxyphenyl)perfluorooct-1-ene as a colorless liquid in 87% (0.680 g, 1.4 mmol) yield. <sup>19</sup>F NMR (CDCl<sub>3</sub>):  $\delta$  –81.3 (t, *J* = 10 Hz, 3F, *CF*<sub>3</sub>–), –98.4 (d, *J* = 11 Hz, 1F, Ar-*CF*=), –113.5 (q, *J* = 13 Hz, 2F, *CF*<sub>2</sub>–), –122.5 (m, 4F, 2*CF*<sub>2</sub>–), –123.2 (m, 2F, *CF*<sub>2</sub>–), –126.6 (m, 2F, *CF*<sub>2</sub>–), –152.8 (m, 1F, R<sub>F</sub>-*CF*=). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.38 (d, *J* = 7.6 Hz, 2H), 6.93 (d, *J* = 8.6 Hz, 2H), 3.84 (s, 3H); GC/MS: 488 (*M*<sup>+</sup>, 14), 469 (67), 219 (100, BP), 199 (35), 69 (22); HRMS: calcd. for C<sub>15</sub>H<sub>7</sub>F<sub>15</sub>O 488.0257, found 488.0262.

## 3.6.5. (Z)-1-(2-Methylphenyl)perfluorooct-1-ene $[2-MeC_6H_4CF=CFC_6F_{13}]$

The perfluorooctenylzinc reagent solution  $[C_6F_{13}CF=C]$ FZnCl] (2.7 mmol), 2-iodotoluene (0.350 g, 1.6 mmol) and  $Pd(PPh_3)_4$  (0.030 g) were heated at 65 °C for 18 h. Trituration of the reaction mixture with hexane followed by purification of the crude product by chromatography (eluent: hexane) produced the (Z)-1-(2-methylphenyl)perfluorooct-1-ene as a colorless liquid in 78% (0.588 g, 1.3 mmol) yield. <sup>19</sup>F NMR (CDCl<sub>3</sub>):  $\delta$  -81.3 (t, J = 10.8 Hz, 3F, CF<sub>3</sub>-), -99.0 (d, J = 12.3 Hz, 1F, Ar-CF =), -114.5 (q, J = 12.1 Hz, 2F,  $CF_{2}$ -), -122.6 (m, 2F, CF<sub>2</sub>-), -122.8 (m, 2F, CF<sub>2</sub>-), -123.3 (m, 2F,  $CF_{2}$ -), -126.6 (m, 2F,  $CF_{2}$ -), -152.2 (m, 1F, R<sub>F</sub>-CF=). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.42 (m, 1H), 7.29–7.20 (m, 3H), 2.38 (d, J = 2.7 Hz; GC/MS: 472 ( $M^+$ , 65), 453 (20), 204 (37), 203 (100, BP), 183 (78), 153 (45), 151 (67), 134 (60), 133 (86), 119 (27), 69 (65); HRMS: calcd. for C15H7F15 472.0308, found 472.0304.

# 3.7. Synthesis of the perfluorododecenylzinc reagent $[n-C_{10}F_{21}CF=CFZnCl]$ and 1-arylperfluoro-1-dodecene $[n-C_{10}F_{21}CF=CFAr]$

Following the standard procedure for the preparation of perfluoroalkenylzinc reagents, metallation of 1H,1H-perfluorododecane (10.5 g, 17.0 mmol) with LDA (37.0 mmol) in presence of ZnCl<sub>2</sub> (2.3 g, 17.0 mmol) at 0 °C in THF-ether medium (140 mL, 1:1) produced [C<sub>10</sub>F<sub>21</sub>CF=CFZnCl] as a brown solution in 61% yield.

### 3.7.1. (Z)- and (E)-1-phenylperfluorododec-1-ene $[C_6H_5CF=CFC_{10}F_{21}]$

The perfluorododecenylzinc reagent solution  $[C_{10}F_{21}CF=C$  FZnCl] (2.09 mmol), iodobenzene (0.245 g, 1.2 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.030 g) were heated at 65 °C for 12 h. Trituration of the reaction mixture with hexane followed by purification of the crude product by chromatography (eluent: hexane) afforded a mixture of (*E*)- and (*Z*)-1-phenylperfluorododec-1-ene (*Z/E* 94:6) as a colorless solid in 78% (0.616 g, 0.936 mmol) yield. <sup>19</sup>F NMR (CDCl<sub>3</sub>):  $\delta$  -81.2 (t, *J* = 10 Hz, 3F, *CF*<sub>3</sub>–), -99.9 (d, *J* = 8 Hz, 1F, Ar-*CF*=), -113.6 (m, 2F, *CF*<sub>2</sub>–), -122.2 (m, 12F, 6*CF*<sub>2</sub>–), -123.2 (m, 2F, *CF*<sub>2</sub>–), -126.6 (m, 2F, *CF*<sub>2</sub>–), -152.2 (m, 1F, R<sub>F</sub>-*CF*=). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.53–7.44 (m, 5H, Ar*H*); GC/MS: 658 (*M*<sup>+</sup>, 11), 639 (7), 189 (100, BP), 169 (75), 69 (27); HRMS: calcd. for C<sub>18</sub>H<sub>5</sub>F<sub>23</sub> 658.0024, found 658.0026.

#### 3.7.2. (*Z*)- and (*E*)-1-(3trifluoromethylphenyl)perfluorododec-1-ene $[3-CF_3C_6H_4CF=CFC_{10}F_{21}]$

The perfluorododecenylzinc reagent solution [C<sub>10</sub>F<sub>21</sub>CF=C (2.09 mmol), 3-iodobenzotrifluoride FZnCl] (0.326 g, 1.2 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.030 g) were heated at 65  $^{\circ}$ C for 12 h. Trituration of the reaction mixture with hexane followed by purification of the crude product by chromatography (eluent: hexane) afforded a mixture of (E)- and (Z)-1-(3-trifluoromethylphenyl)perfluorododec-1-ene (Z/E 93:8) as a colorless waxy solid in 82% (0.713 g, 0.983 mmol) yield. <sup>19</sup>F NMR (CDCl<sub>3</sub>):  $\delta$  -63.7 (s, 3F, Ar-*CF*<sub>3</sub>), -81.4 (t, *J* = 11 Hz, 3F,  $CF_{3}$ -), -102.0 (d, J = 7 Hz, 1F, Ar-CF=), -113.9 (m, 2F, *CF*<sub>2</sub>-), -122.3 (m, 12F, 6*CF*<sub>2</sub>-), -123.4 (m, 2F, *CF*<sub>2</sub>-), -126.7 (m, 2F, CF<sub>2</sub>-), -149.7 (m, 1F, R<sub>F</sub>-CF=). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.80 (d, J = 7 Hz, 1H), 7.72 (s, 1H), 7.64 (t, distorted, 1H), 7.58 (d, distorted, 1H); GC/MS: 726 (M<sup>+</sup>, 3), 707 (3), 257 (100, BP), 237 (60), 187 (30), 169 (50), 119 (32), 69 (78); HRMS: calcd. for C<sub>19</sub>H<sub>4</sub>F<sub>26</sub> 725.9898, found 725.9894.

### 3.7.3. (Z)- and (E)-1-(3-fluorophenyl)perfluorododec-1-ene $[3-FC_6H_4CF=CFC_{10}F_{21}]$

The perfluorododecenylzinc reagent solution  $[C_{10}F_{21}CF=C$ FZnCl] (2.09 mmol), 3-fluoroiodobenzene (0.266 g, 1.2 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.030 g) were heated at 65 °C for 12 h. Trituration of the reaction mixture with hexane followed by purification of the crude product by chromatography (eluent: hexane) afforded a mixture of (*E*)- and (*Z*)-1-(3-fluorophenyl)perfluorododec-1-ene (*Z*/*E* 92:8) as a colorless viscous oil in 72% (0.585 g, 0.865 mmol) yield. <sup>19</sup>F NMR (CDCl<sub>3</sub>):  $\delta$  -81.3 (t, *J* = 10 Hz, 3F, *CF*<sub>3</sub>-), -101.3 (d, *J* = 9 Hz, 1F, Ar-*CF*=), -111.9 (m, 1F, Ar*F*-), -113.9 (m, 2F, *CF*<sub>2</sub>-), -122.3 (m, 12F, 6*CF*<sub>2</sub>-), -123.2 (m, 2F, *CF*<sub>2</sub>-), -126.6 (m, 2F, *CF*<sub>2</sub>-), -150.6 (m, 1F, R<sub>F</sub>-*CF*=). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.44 (m, 1H), 7.26–7.16 (m, 3H); GC/MS: 676 ( $M^{+}$ , 7), 657 (5), 207 (100, BP), 187 (71), 169 (22), 69 (44); HRMS: calcd. for C<sub>18</sub>H<sub>4</sub>F<sub>24</sub> 675.9930, found 675.9934.

### 3.7.4. (Z)- and (E)-1-(4-methoxyphenyl)perfluorododec-1ene $[4-MeOC_6H_4CF=CFC_{10}F_{21}]$

The perfluorododecenylzinc reagent solution  $[C_{10}F_{21}CF=C$  FZnCl] (2.09 mmol), 4-iodoanisole (0.281 g, 1.2 mmol) and

Pd(PPh<sub>3</sub>)<sub>4</sub> (0.030 g) were heated at 65 °C for 10 h. Trituration of the reaction mixture with hexane followed by purification of the crude product by chromatography (eluent: 5% CH<sub>2</sub>Cl<sub>2</sub>– hexane) afforded a mixture of (*E*)- and (*Z*)-1-(4-methoxyphenyl)perfluorododec-1-ene (*Z*/*E* 93:7) as a pale yellow waxy solid in 76% (0.898 g, 0.914 mmol) yield. <sup>19</sup>F NMR (CDCl<sub>3</sub>): δ –81.3 (t, *J* = 11 Hz, 3F, *CF*<sub>3</sub>–), –98.4 (d, *J* = 11 Hz, 1F, Ar-*CF*=), –113.5 (q, *J* = 14 Hz, 2F, *CF*<sub>2</sub>–), –122.2 (m, 12F, 2*CF*<sub>2</sub>–), –123.5 (m, 2F, *CF*<sub>2</sub>–), –126.6 (m, 2F, *CF*<sub>2</sub>–), –152.9 (m, 1F, R<sub>F</sub>-*CF*=). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.38 (d, *J* = 8 Hz, 2H), 6.94 (d, *J* = 9 Hz, 2H), 3.58 (s, 3H); GC/MS: 688 (*M*<sup>+</sup>, 18), 669 (15), 219 (100, BP), 199 (27), 69 (26); HRMS: calcd. for C<sub>19</sub>H<sub>7</sub>F<sub>23</sub>O 688.0130, found 688.0132.

#### 3.8. Synthesis of (E)-1-iodoperfluoroalkenes

#### 3.8.1. (E)-1-Iodoperfluorohept-1-ene ( $C_5F_{11}CF=CFI$ )

The perfluoroheptenylzinc reagent [C<sub>5</sub>F<sub>11</sub>CF=CFZnCl] was prepared at -78 °C by the metallation of 1H,1H-perfluoroheptane (3.05 g, 8.6 mmol) with LDA (18.9 mmol) in presence of ZnCl<sub>2</sub> (1.16 g, 8.6 mmol) as per the general procedure. The reaction mixture was concentrated to half its volume under vacuum and guenched with iodine (2.18 g, 8.6 mmol). Diethyl ether (50.0 mL) was added to the reaction mixture and the organic layer washed with water  $(2 \times 25 \text{ mL})$ , dried (anhy. Na<sub>2</sub>SO<sub>4</sub>) and the solvents were removed under mild vacuum in a rotavaopur. The crude product was distilled under reduced pressure to afford pure cis-1-iodoperfluorohept-1-ene as a colorless liquid (2.69 g, 5.9 mmol, 68%) [bp: 50-51 °C/20 mmHg]. <sup>19</sup>F NMR (CDCl<sub>3</sub>):  $\delta$  –81.3 (t, J = 11 Hz, 3F,  $CF_{3-}$ ), -82.3 (d, J = 9 Hz, 1F, I-CF =), -113.8 (m, 2F,  $CF_{2-}$ ), -123.1 (m, 2F, CF<sub>2</sub>-), -123.4 (m, 2F, CF<sub>2</sub>-), -126.7 (m, 2F,  $CF_{2}$ -), -128.8 (m, 1F, R<sub>F</sub>-CF=); HRMS: calcd. for C<sub>7</sub>F<sub>13</sub>I 457.8837, found 457.8837.

#### 3.8.2. (E)-1-Iodoperfluorooct-1-ene ( $C_6F_{13}CF=CFI$ )

The perfluorooctenylzinc reagent [C<sub>6</sub>F<sub>13</sub>CF=CFZnCl] was generated at -78 °C by the metallation of 1*H*,1*H*-perfluorooctane (2.59 g, 6.5 mmol) with LDA (14.2 mmol) in presence of ZnCl<sub>2</sub> (0.878 g, 6.46 mmol) as per the general procedure. Addition of iodine (1.64 g, 6.46 mmol) followed by work-up and purification by distillation afforded pure *cis*-1-iodoperfluoroct-1-ene as a colorless liquid (2.30 g, 4.5 mmol, 70%) [71] [bp: 67–70 °C/24 mmHg]. <sup>19</sup>F NMR (CDCl<sub>3</sub>):  $\delta$  –81.3 (t, J = 11 Hz, 3F,  $CF_{3-}$ ), -82.3 (d, J = 9 Hz, 1F, I-CF=), -113.7 (m, 2F,  $CF_{2-}$ ), -122.2 (m, 2F,  $CF_{2-}$ ), -122.8 (m, 2F,  $CF_{2-}$ ), -123.3 (m, 2F,  $CF_{2-}$ ), -126.6 (m, 2F,  $CF_{2-}$ ), -128.7 (m, 1F, R<sub>F</sub>-CF=); HRMS: calcd. for C<sub>8</sub>F<sub>15</sub>I 507.8805, found 507.8804.

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