

# Sodium dithionite initiated addition of $\text{CF}_2\text{Br}_2$ , $\text{CF}_3\text{I}$ and $(\text{CF}_3)_2\text{CFI}$ to allylaromatics Synthesis and the reactivity of 4-aryl-1,1-difluorodienes and 4-aryl-1,1-bis(trifluoromethyl)dienes

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## Abstract

Sodium dithionite initiated addition of  $\text{CF}_2\text{Br}_2$ ,  $\text{CF}_3\text{I}$  and  $(\text{CF}_3)_2\text{CFI}$  to the terminal double bond of allylbenzenes and of  $(\text{CF}_3)_2\text{CFI}$  to allylpyridines in a MeCN/ $\text{H}_2\text{O}$  system were investigated. The reactions of  $\text{CF}_2\text{Br}_2$  with allylbenzenes gave comparable amounts of adducts, 1-(2,4-dibromo-4,4-difluorobutyl)benzenes, debrominated products, 1-(4-bromo-4,4-difluorobutyl)benzenes, and dimeric compounds in total yields 40–66%. Treatment of the adducts with DBU resulted in double dehydrohalogenation affording 4-aryl-1,1-difluorobutadienes which undergo Diels–Alder condensation with nitrogen dienophiles to give *N*-heterocycles with difluoromethylene group in the ring. The reactions of  $\text{CF}_3\text{I}$  and  $(\text{CF}_3)_2\text{CFI}$  with allylbenzenes gave the respective adducts, (4,4,4-trifluoro-2-iodobutyl)benzenes and 1-(4,5,5,5-tetrafluoro-4-(trifluoromethyl)-2-iodopentyl)benzenes as the main products. Dehydrohalogenation of these adducts resulted, respectively, in (4,4,4-trifluoro-but-1-enyl)benzenes and 4-aryl-1,1-bis(trifluoromethyl)butadienes in high yields.  $(\text{CF}_3)_2\text{CFI}$  reacted rapidly with allylpyridines to give mixtures from which, after treatment with DBU, 4-pyridyl-1,1-bis(trifluoromethyl)butadienes were isolated in a ca. 60% yield.

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**Keywords:** Dibromodifluoromethane; Trifluoroiodomethane; 2-Iodoheptafluoropropane; Radical addition; Sodium dithionite; Allylaromatics; 1,1-Difluorodienes; 1,1-Bis(trifluoromethyl)dienes

## 1. Introduction

In the preceding paper we reported the sodium dithionite initiated additions of 1-bromo-1-chloro-2,2,2-trifluoroethane (Halothane<sup>®</sup>) to a number of allylaromatics [1]. Dehydrohalogenation of the resulting (2-bromo-4-chloro-5,5,5-trifluoropentyl)benzenes afforded high yields of conjugated dienes terminated with the  $\text{CF}_3$  group at the one end and an aryl group at the other. With the aim to extend this method to the synthesis of dienes terminated with the  $\text{CF}_2$  group (1,1-difluorodienes) we investigated sodium dithionite initiated additions of dibromodifluoromethane and trifluoroiodomethane to allylbenzenes and dehydrohalogenation of the adducts. Although such reactions have been previously studied by Elsheimer et al. [2],

CuCl and ethanolamine were used as initiators for the additions, reactions with allylbenzenes were limited to only two examples and yields were rather low. Nevertheless, the work by Elsheimer has shown that 1,1-difluorodienes are very active in the 4 + 2 cycloadditions what additionally prompted us to look for a new method of their synthesis. Synthesis of dienes terminated with two geminal  $\text{CF}_3$  groups, via additions of 2-iodoheptafluoropropane to allylaromatics, and reactivity of such dienes were also investigated.

## 2. Results and discussion

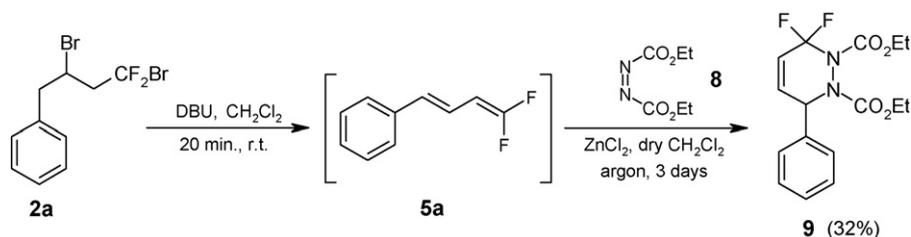
### 2.1. Reactions involving $\text{CF}_2\text{Br}_2$

The reactions of dibromodifluoromethane with allylbenzenes **1**, because of the volatility of the former, were carried out in a closed system (pressure glass ampoule). Water–acetonitrile solution (1: 1 by volume) was used as the reaction medium in

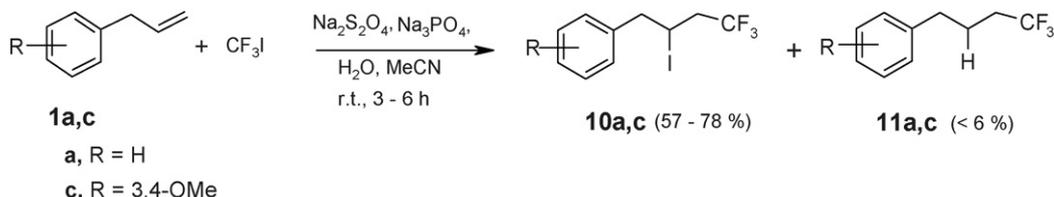
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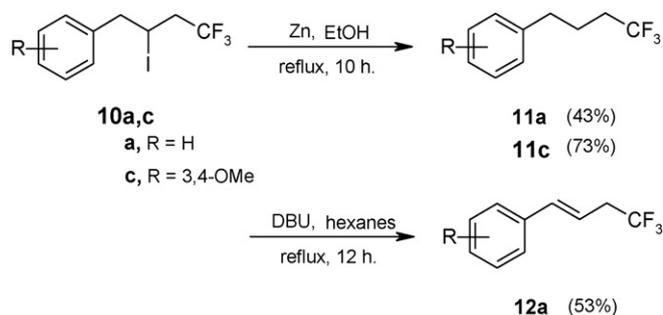




Scheme 3.



Scheme 4.



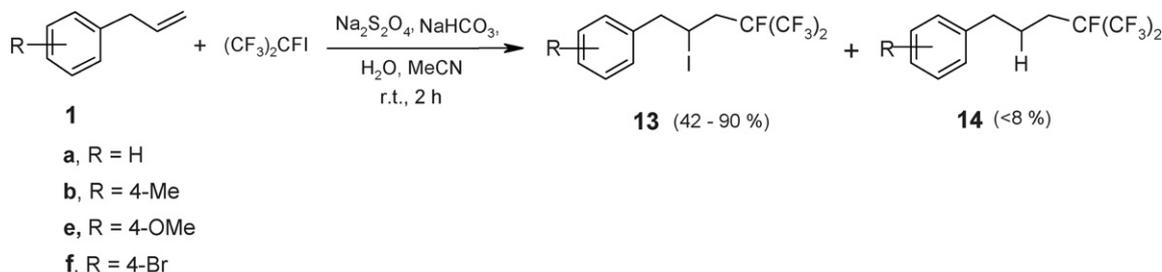
Scheme 5.

reactions of diene **5a** with common dienophiles like maleic anhydride, diethyl acetylenedicarboxylate, *cis*-1,2-bis(phenylsulphonyl)ethylene and others, failed because decomposition of the diene occurred faster than the cycloaddition reaction.

In conclusion, although dehydrobromination of adducts **2** gives acceptable yields of highly reactive 1,1-difluorodienes **5** (as determined by cycloaddition reactions), low yields of these adducts in the sodium dithionite initiated reactions of allylbenzenes with  $\text{CF}_2\text{Br}_2$  makes this procedure of little practical value.

## 2.2. Reactions involving $\text{CF}_3\text{I}$

The reactions of trifluoroiodomethane with allylbenzenes **1**, as those with  $\text{CF}_2\text{Br}_2$ , were carried out in a closed system



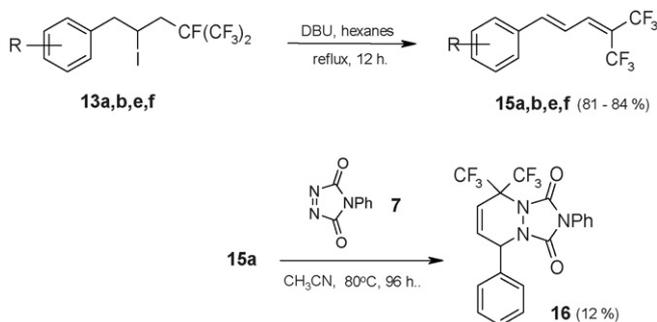
Scheme 6.

(pressure glass ampoule), under similar conditions. The reactions proceeded cleanly to give adducts, (4,4,4-trifluoro-2-iodobutyl)benzenes (**10**), as the main products with only negligible amounts of reductively deiodinated compounds **11** (Scheme 4).

The identity of minor compound **11** was confirmed by comparison of weak signals in the NMR spectra of mixtures of products **10** + **11** with the spectra of pure compounds **11** which were obtained by treatment of these mixtures with zinc metal in ethanol. Unfortunately, adducts **10** on treatment with DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) eliminate only HI molecule to give (4,4,4-trifluoro-but-1-enyl)benzenes **12** (Scheme 5). The attempted simultaneous elimination of HF to form 1,1-difluorodienes **5** failed, even by treatment with very strong bases like LDA or *t*-BuOK.

## 2.3. Reactions involving $(\text{CF}_3)_2\text{CFI}$

These reactions were carried out in an open system under standard conditions using  $\text{NaHCO}_3$  as the HI scavenger. The reactions proceeded readily at ambient temperature to give in most cases high yields of the expected adducts, 1-(4,5,5,5-tetrafluoro-4-(trifluoromethyl)-2-iodopentyl)benzenes (**13**) (Scheme 6). Deiodinated compounds **14** were formed in only insignificant amounts. Similarly to compounds **11**, the identity of minor compounds **14** was confirmed by comparison of weak signals in the NMR spectra of the crude reaction mixtures with



Scheme 7.

the  $^1\text{H}$  NMR and  $^{19}\text{F}$  NMR spectra of pure compound **14a**, which was obtained by treatment of a mixtures of **13** + **14** with zinc metal in ethanol.

The best result was achieved in the reaction of  $(\text{CF}_3)_2\text{CFI}$  with 4-methoxyallylbenzene **1e** which gave a 90% yield of isolated adduct **13e** and, as expected, the bromo-substituted adduct **13f** was obtained in the lowest yield (42%).

Adducts **13** on treatment with DBU eliminate both HI and HF to give high yields of conjugated dienes **15** terminated with two  $\text{CF}_3$  groups (Scheme 7), which were easily isolated by column chromatography. The  $^1\text{H}$  NMR spectra of dienes **15** revealed that they are formed exclusive as the *trans*-form ( $J_{\text{HH}}^{\text{trans}} = \text{ca. } 15 \text{ Hz}$ ). These dienes were found to be very stable and unreactive. Prolonged heating with common dienophiles (maleic anhydride, diethyl acetylenedicarboxylate) do not lead to any products; both substrates were recovered unchanged. Even the reaction of **15a** with 4-phenyl-3*H*-1,2,4-triazoline-3,5-dione (**7**) conducted at  $80^\circ\text{C}$  for 96 h resulted in only 12% conversion to cycloadduct **16** (not isolated).

In contrast to sluggish reactions with  $\text{CF}_3\text{CHClBr}$  reported earlier [1],  $(\text{CF}_3)_2\text{CFI}$  reacts with 2- and 3-allylpyridines **17** rapidly at ambient temperature to give complex mixtures of products. Initial cooling was necessary to control the rates of these reactions and to achieve better yields of the supposed adducts **18**. These adducts were expected to be not stable and therefore their isolation was not attempted. The crude reaction mixtures were treated with DBU to give mixtures from which 1,1-bis(trifluoromethyl)dienes **19** were isolated in 58–60% yield (Scheme 8).

It has been reported [3] that unsubstituted 1,1-bis(trifluoromethyl)butadiene behaves like an electrophilic alkene rather

than like a diene and undergoes 4 + 2 cycloadditions with dienes. However, the attempted reactions of compounds **15** and **19** with various nucleophilic reagents, including dienes, also failed.

### 3. Experimental

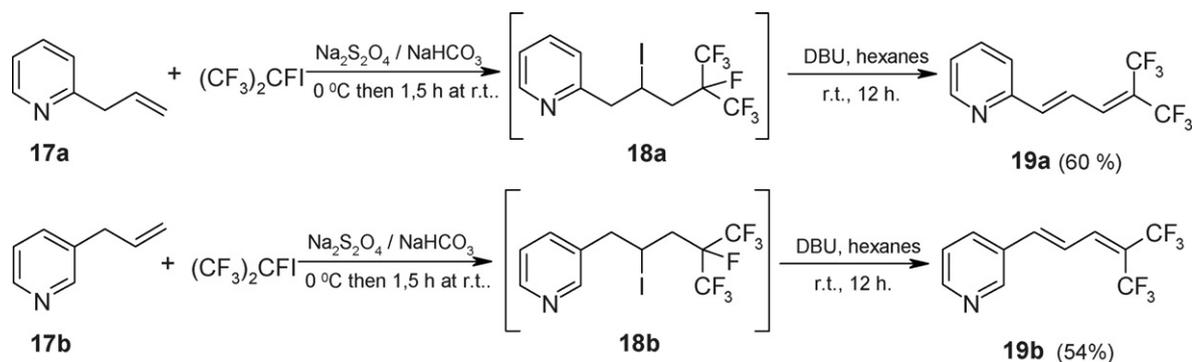
Melting points were determined in capillaries and are uncorrected.  $^1\text{H}$  NMR,  $^{19}\text{F}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded (at 400, 376 and 100 MHz, respectively) with a Varian 400 spectrometer in  $\text{CDCl}_3$  solutions (or as indicated otherwise). Chemical shifts are quoted in ppm from internal TMS for  $^1\text{H}$  and  $^{13}\text{C}$  and from internal  $\text{CFCl}_3$  for  $^{19}\text{F}$  nuclei. Coupling constants ( $J$ ) values are in Hz. GC–MS analyses were performed with a Hewlett–Packard 5890 apparatus (30 m capillary column, HP-5 oil). Mass spectra of pure compounds were obtained with an AMD-604 spectrometer.

Dibromodifluoromethane, trifluoroiodomethane, heptafluoro-2-iodopropane, allylbenzenes **1a**, **1c**, and **1e**, and diethyl azodicarboxylate were commercial reagents. Other allylbenzenes and allylpyridines were prepared by allylation of the appropriate magnesium aryl bromides with allylbromide [4–7]. 4-Phenyl-3*H*-1,2,4-triazoline-3,5-dione was prepared according to the literature procedure [8].

#### 3.1. Addition of $\text{CF}_2\text{Br}_2$ to allylbenzenes

##### 3.1.1. Addition of $\text{CF}_2\text{Br}_2$ to allylbenzene (**1a**)

A pressure glass ampoule (150 ml) fitted with a Rotaflo<sup>®</sup> valve and magnetic stirring bar was filled with a water–acetonitrile solution (1:1, 60 ml), sodium dithionite (2.5 g, 12 mmol [85%]),  $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$  (7.0 g, 18 mmol), allylbenzene (**1a**) (1.5 g, 12 mmol) and dibromodifluoromethane (2.9 g, 14 mmol). The ampoule was closed and vigorously stirred at ambient temperature ( $20\text{--}25^\circ\text{C}$ ) for 3 h after which water was added (20 ml), the reaction mixture was extracted with diethyl ether ( $3 \times 50 \text{ ml}$ ) and the combined extract were dried over  $\text{MgSO}_4$ . The crude mixture of products obtained after evaporation of the solvent (3.06 g, yellowish oil) was subjected to column chromatography (silica gel, hexanes) to give compounds **2a**, **3a** and **4a**. Usually, 1:1 ratios of  $\text{Na}_2\text{S}_2\text{O}_4$  to alkenes **1** were used but decreased  $\text{Na}_2\text{S}_2\text{O}_4/\mathbf{1}$  ratio does not diminish formation of compounds **3** and **4**.



Scheme 8.

(2,4-Dibromo-4,4-difluorobutyl)benzene (**2a**): yield: 0.65 g (16%). Colorless liquid.  $^1\text{H}$  NMR: 3.01 (complex AB system,  $^2J_{\text{HH}} = 14.4$ , 2H); 3.17 (dd,  $^2J_{\text{HH}} = 14.4$ ;  $^3J_{\text{HH}} = 8.0$ , 1H); 3.28 (dd,  $^2J_{\text{HH}} = 14.4$ ;  $^3J_{\text{HH}} = 6.0$ , 1H); 4.41 (dq,  $^3J_{\text{HH}} = ^3J_{\text{HH}} = \text{ca. } 7.9$ ;  $^3J_{\text{HH}} = ^3J_{\text{HH}} = \text{ca. } 6.2$ , 1H); 7.22 (d,  $^3J_{\text{HH}} = 8.0$ , 2H); 7.29 (m, 1H); 7.35 (m, 2H).  $^{19}\text{F}$  NMR:  $-42.4$  (ddd,  $^2J_{\text{FF}} = 158.2$ ,  $^3J_{\text{FH}} = 14.2$ ;  $^3J_{\text{FH}} = 11.8$ , 1F);  $-43.5$  (ddd,  $^2J_{\text{FF}} = 158.2$ ;  $^3J_{\text{FH}} = 14.5$ ;  $^3J_{\text{FH}} = 13.0$ , 1F). MS (EI):  $m/z$  (rel. int., ion): 330, 328, 326 (10, 22, 12,  $M^+$ ); 297 [ $<1$ , ( $M - \text{C}_6\text{H}_5$ ) $^+$ ]; 249, 247 [4, 4, ( $M - \text{Br}$ ) $^+$ ]; 248, 246 [5, 1, ( $M - \text{HBr}$ ) $^+$ ]; 229, 227 [16, 17, ( $\text{C}_{10}\text{H}_9\text{BrF}$ ) $^+$ ]; 215 (1); 195 (1); 185, 183 [10, 10 ( $M - \text{CH}_2\text{CF}_2\text{Br}$ ) $^+$ ]; 167 [34, ( $\text{C}_{10}\text{H}_9\text{F}_2$ ) $^+$ ]; 147 [64, ( $\text{C}_{10}\text{H}_8\text{F}$ ) $^+$ ]; 127 (12); 117 (11); 115 (12); 104 [14, ( $\text{C}_8\text{H}_8$ ) $^+$ ]; 91 [100, ( $\text{C}_7\text{H}_7$ ) $^+$ ]. Analysis: found: C, 37.0; H, 3.3; F, 11.7; Br, 48.4%. Calculated for  $\text{C}_{10}\text{H}_{10}\text{F}_2\text{Br}_2$  (327.99): C, 36.6; H, 3.1; F, 11.6; Br, 48.7%. HRMS: found: 325.91119. Calculated for  $\text{C}_{10}\text{H}_{10}\text{F}_2^{79}\text{Br}_2$ : 325.91173.

(4-Bromo-4,4-difluorobutyl)benzene (**3a**): yield: 0.52 g (17%). Colorless liquid.  $^1\text{H}$  NMR: 1.91–2.01 (m, 2H); 2.69 (t,  $^3J_{\text{HH}} = 7.5$ , 2H); 2.29–2.41 (m,  $^3J_{\text{HF}} = 13.7$ , 2H); 7.15–7.20 (m, 2H); 7.20–7.24 (m, 1H); 7.28–7.33 (m, 2H).  $^{19}\text{F}$  NMR:  $-43.8$  (t,  $^3J_{\text{FH}} = 13.7$ , 2F). MS (EI):  $m/z$  (rel. int., ion): 250, 248 (56, 57,  $M^+$ ); 169 [20, ( $M - \text{Br}$ ) $^+$ ]; 149 [55, ( $\text{C}_{10}\text{H}_{10}\text{F}$ ) $^+$ ]; 127 (10); 105 [16, ( $\text{C}_8\text{H}_9$ ) $^+$ ]; 91 [100, ( $\text{C}_7\text{H}_7$ ) $^+$ ]. Analysis: found: C, 48.2; H, 4.2; F, 15.2; Br, 32.2%. Calculated for  $\text{C}_{10}\text{H}_{11}\text{F}_2\text{Br}$  (249.10): C, 48.2%; H, 4.4%; F, 15.2%; Br, 32.1%.

2,3-Bis(2-bromo-2,2-difluoroethyl)-1,4-diphenylbutane (**4a**): yield: 0.69 g (11%). Viscous resin.  $^1\text{H}$  NMR: 2.28 (m, 3H); 2.46 (m, 3H); 2.66 (complex AB system, 3H); 2.82 (dd,  $^2J_{\text{HH}} = 14.1$ ;  $^3J_{\text{HH}} = 7.0$ , 1H); 7.02 (m, 2H); 7.12 (m, 2H); 7.23 (m, 4H); 7.31 (m, 2H).  $^{19}\text{F}$  NMR:  $-40.6$  (ddd,  $^2J_{\text{FF}} = 157.6$ ;  $^3J_{\text{FH}} = \text{ca. } 16.5$ ;  $^3J_{\text{FH}} = \text{ca. } 11.9$ , 1F);  $-42.0$  (dt,  $^2J_{\text{FF}} = 157.6$ ;  $^3J_{\text{FH}} = \text{ca. } 15.0$ , 1F);  $-41.3$  (dt,  $^2J_{\text{FF}} = 157.2$ ;  $^3J_{\text{FH}} = 14.0$ , 1F);  $-41.8$  (dt,  $^2J_{\text{FF}} = 157.2$ ;  $^3J_{\text{FH}} = 14.0$ , 1F).  $^{13}\text{C}$  NMR: 36.1 (s,  $\text{CH}_2$ ); 36.18 (s,  $\text{CH}_2$ ); 36.96 (s, CH); 37.0 (s, CH); 44.18 (t,  $^3J_{\text{CF}} = 20.7$  Hz,  $\text{CH}_2$ ); 44.2 (t,  $^3J_{\text{CF}} = 20.7$  Hz,  $\text{CH}_2$ ); 122.7 (2  $\times$  t,  $^1J_{\text{CF}} = 306.5$  Hz,  $\text{CF}_2\text{Br}$ ); 126.5 (s,  $\text{CH}_{\text{arom.}}$ ); 126.7 (s,  $\text{CH}_{\text{arom.}}$ ); 128.5 (s,  $\text{CH}_{\text{arom.}}$ ); 128.7 (s,  $\text{CH}_{\text{arom.}}$ ); 128.9 (s,  $\text{CH}_{\text{arom.}}$ ); 129.03 (s,  $\text{CH}_{\text{arom.}}$ ); 138.5 (s,  $\text{C}_{\text{arom.}}$ ); 138.6 (s,  $\text{C}_{\text{arom.}}$ ).  $^{13}\text{C}$  NMR DEPT 135:  $-36.1$  (s,  $\text{CH}_2$ );  $-36.2$  (s,  $\text{CH}_2$ ); 36.9 (s, CH); 37.0 (s, CH);  $-44.2$  (t,  $^3J_{\text{CF}} = 20.7$  Hz,  $\text{CH}_2$ );  $-44.2$  (t,  $^3J_{\text{CF}} = 20.7$  Hz,  $\text{CH}_2$ ); 126.5 (s,  $\text{CH}_{\text{arom.}}$ ); 126.7 (s,  $\text{CH}_{\text{arom.}}$ ); 128.5 (s,  $\text{CH}_{\text{arom.}}$ ); 128.7 (s,  $\text{CH}_{\text{arom.}}$ ); 128.9 (s,  $\text{CH}_{\text{arom.}}$ ); 129.0 (s,  $\text{CH}_{\text{arom.}}$ ). MS (EI):  $m/z$  (rel. int., ion): 498, 496, 494 (8, 16, 8,  $M^+$ ); 418 ( $<1$ ); 377, 375 [1, 1, ( $\text{C}_{20}\text{H}_{18}\text{F}_2\text{Br}$ ) $^+$ ]; 289, 287 [1, 1, ( $\text{C}_{13}\text{H}_{14}\text{F}_2\text{Br}$ ) $^+$ ]; 275, 273 [1, 1, ( $\text{C}_{12}\text{H}_{12}\text{F}_2\text{Br}$ ) $^+$ ]; 259 (1); 249 (3); 229 (1); 181 [4, ( $\text{C}_{11}\text{H}_{11}\text{F}_2$ ) $^+$ ]; 159 [2, ( $\text{C}_{12}\text{H}_{15}$ ) $^+$ ]; 147 (8); 117 (8); 105 (3); 91 [100, ( $\text{C}_7\text{H}_7$ ) $^+$ ]. Analysis: found: C, 48.3; H, 4.2; Br, 32.4; F, 15.1%. Calculated for  $\text{C}_{20}\text{H}_{20}\text{F}_4\text{Br}_2$  (496.17): C, 48.4; H, 4.1; Br, 32.2; F, 15.3%. HRMS: found: 493.98763. Calculated for  $\text{C}_{20}\text{H}_{20}\text{F}_4^{79}\text{Br}_2$ : 493.98679.

### 3.1.2. Addition of $\text{CF}_2\text{Br}_2$ to 4-methylallylbenzene (**1b**)

4-Methylallylbenzene (**1b**) (1.0 g, 7.5 mmol),  $\text{CF}_2\text{Br}_2$  (1.9 g, 9 mmol),  $\text{Na}_2\text{S}_2\text{O}_4$  (1.6 g, 7.5 mmol), and  $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$  (4.2 g, 11 mmol) were reacted at ambient temperature for 2 h and worked up as in Section 3.1.1.

1-(2,4-Dibromo-4,4-difluorobutyl)-4-methylbenzene (**2b**): yield: 0.54 g (21%). Colorless liquid.  $^1\text{H}$  NMR: 2.34 (s, 3H); 3.0 (complex AB system, 2H); 3.14 (dd,  $^2J_{\text{HH}} = 14.5$ ;  $^3J_{\text{HH}} = 8.0$ , 1H); 3.23 (dd,  $^2J_{\text{HH}} = 14.5$ ;  $^3J_{\text{HH}} = 6.2$ , 1H); 4.39 (dq,  $^3J_{\text{HH}} = ^3J_{\text{HH}} = \text{ca. } 7.8$ ;  $^3J_{\text{HH}} = ^3J_{\text{HH}} = \text{ca. } 6.3$ , 1H); 7.11 (d,  $^3J_{\text{HH}} = 8.1$ , 2H); 7.15 (d,  $^3J_{\text{HH}} = 8.1$  Hz, 2H).  $^{19}\text{F}$  NMR:  $-42.3$  (dt,  $^2J_{\text{FF}} = 158.0$  Hz;  $^3J_{\text{FH}} = \text{ca. } 13.2$  Hz, 1F);  $-43.5$  (dt,  $^2J_{\text{FF}} = 158.0$ ;  $^3J_{\text{FH}} = 13.8$ , 1F). MS:  $m/z$ , (rel. int., ion): 344, 342, 340 (6, 13, 6,  $M^+$ ); 263, 261 [1, 1, ( $M - \text{Br}$ ) $^+$ ]; 264, 262 [3, 3 ( $M - \text{HBr}$ ) $^+$ ]; 241 [1, ( $\text{C}_{11}\text{H}_{11}\text{FBr}$ ) $^+$ ]; 199, 197 [1, 1, ( $M - \text{CH}_2\text{CF}_2\text{Br}$ ) $^+$ ]; 182 [14, ( $M - 2\text{Br}$ ) $^+$ ]; 167 (6); 161 (6); 146 (4); 131 (3); 117 (4); 105 [100, ( $\text{C}_8\text{H}_9$ ) $^+$ ]; 91 [5, ( $\text{C}_7\text{H}_7$ ) $^+$ ]. HRMS: found: 339.92835. Calculated for  $\text{C}_{11}\text{H}_{12}\text{F}_2^{79}\text{Br}_2$ : 339.92738.

1-(4-Bromo-4,4-difluorobutyl)-4-methylbenzene (**3b**): yield: 0.31 g (16%). Colorless liquid.  $^1\text{H}$  NMR: 1.94 (m, 2H); 2.32 (s, 3H); 2.36 (m, 2H); 2.65 (t,  $^3J_{\text{HH}} = 7.5$ , 2H); 7.07 (d,  $^3J_{\text{HH}} = 7.9$ , 2H); 7.11 (d,  $^3J_{\text{HH}} = 7.9$ , 2H).  $^{19}\text{F}$  NMR:  $-43.8$  (t,  $^3J_{\text{FH}} = 13.9$ , 2F). MS:  $m/z$  (rel. int., ion): 264, 262 (12, 14,  $M^+$ ); 218 (5); 183 [3, ( $M - \text{Br}$ ) $^+$ ]; 163 [7, ( $\text{C}_{11}\text{H}_{12}\text{F}$ ) $^+$ ]; 146 (3); 117 (13); 105 [100, ( $\text{C}_8\text{H}_9$ ) $^+$ ]. HRMS: found: 262.01606. Calculated for  $\text{C}_{11}\text{H}_{13}\text{F}_2^{79}\text{Br}$ : 262.01687.

2,3-Bis(2-bromo-2,2-difluoroethyl)-1,4-bis(4-methylphenyl)butane (**4b**): yield: 0.62 g (16%). Viscous resin.  $^1\text{H}$  NMR: 2.32 (s, 6H); 2.35–2.83 (m, 10H); 6.93 (d,  $^3J_{\text{HH}} = 8.0$ , 2H); 7.01 (d,  $^3J_{\text{HH}} = 8.0$ , 2H); 7.06 (d,  $^3J_{\text{HH}} = 7.7$ , 2H); 7.11 (d,  $^3J_{\text{HH}} = 7.7$ , 2H).  $^{19}\text{F}$  NMR:  $-40.2$  (ddd,  $^2J_{\text{FF}} = 157.4$ ;  $^3J_{\text{FH}} = 16.8$ ;  $^3J_{\text{FH}} = 10.7$ , 1F);  $-41.7$  (m, 2F);  $-42.1$  (dt,  $^2J_{\text{FF}} = 157.4$ ;  $^3J_{\text{FH}} = 15.4$ , 1F). MS:  $m/z$  (rel. int., ion): 526, 524, 522 (2, 4, 2,  $M^+$ ); 393, 391 [1, 2, ( $\text{C}_{21}\text{H}_{22}\text{F}_2\text{Br}$ ) $^+$ ]; 311 [1, ( $\text{C}_{21}\text{H}_{21}\text{F}_2$ ) $^+$ ]; 301 (2); 287 ( $<1$ ); 261 (2); 241 (1); 231 (1); 197 (1); 181 (3); 161 (4); 141 (2); 131 (4); 105 [100, ( $\text{C}_8\text{H}_9$ ) $^+$ ]. Analysis: found: C, 50.7; H, 4.2; Br, 30.2; F, 14.4%. Calculated for  $\text{C}_{22}\text{H}_{24}\text{F}_4\text{Br}_2$  (524.24): C, 50.4; H, 4.6; Br, 30.5; F, 14.5%. HRMS: found: 522.01728. Calculated for  $\text{C}_{22}\text{H}_{24}\text{F}_4^{79}\text{Br}_2$ : 522.01809.

### 3.1.3. Addition of $\text{CF}_2\text{Br}_2$ to 3,4-dimethoxyallylbenzene (**1c**)

3,4-Dimethoxyallylbenzene (**1c**) (0.6 g, 3.3 mmol),  $\text{CF}_2\text{Br}_2$  (0.83 g, 4 mmol),  $\text{Na}_2\text{S}_2\text{O}_4$  (0.7 g, 3.3 mmol), and  $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$  (1.9 g, 5 mmol) were reacted at ambient temperature for 0.5 h and worked up as in Section 3.1.1. Compounds **2c** and **3c** were isolated and identified as a mixture; yield: 0.58 g, **2c**:**3c** = 1.3:1. Colorless liquid.

1-(2,4-Dibromo-4,4-difluorobutyl)-3,4-dimethoxybenzene (**2c**): yield: 26%.  $^1\text{H}$  NMR: 2.98 (dd,  $^3J_{\text{FH}} = 12.9$ ;  $^3J_{\text{HH}} = 6.3$ , 1H); 3.01 (dd,  $^3J_{\text{FH}} = 13.9$ ;  $^3J_{\text{HH}} = 6.7$ , 1H); 3.14 (dd,  $^2J_{\text{HH}} = 14.5$ ;  $^3J_{\text{HH}} = 7.6$ , 1H); 3.21 (dd,  $^2J_{\text{HH}} = 14.5$ ;  $^3J_{\text{HH}} = 6.5$ , 1H); 3.88 (s, 3H); 3.89 (s, 3H); 4.39 (dq,  $^3J_{\text{HH}} = ^3J_{\text{HH}} = \text{ca. } 7.5$ ;  $^3J_{\text{HH}} = ^3J_{\text{HH}} = \text{ca. } 6.7$ ; 1H); 6.67–6.90 (m, overlapping signals of aromatic protons of **2c** and **3c**).  $^{19}\text{F}$  NMR:  $-42.3$  (dt,  $^2J_{\text{FF}} = 157.9$ ;  $^3J_{\text{FH}} = 12.9$ , 1F);  $-43.6$  (dt,  $^2J_{\text{FF}} = 157.9$ ;  $^3J_{\text{FH}} = 13.9$ , 1F). GC-MS:  $m/z$  (rel. int., ion): 390, 388, 386 (4, 7, 4,  $M^+$ ); 209, 207 [3, 3, ( $M - \text{Br}$ ) $^+$ ]; 227 [3, ( $\text{C}_{12}\text{H}_{13}\text{O}_2\text{F}_2$ ) $^+$ ]; 207 [3, ( $\text{C}_{12}\text{H}_{12}\text{O}_2\text{F}$ ) $^+$ ]; 151 [100, ( $\text{C}_9\text{H}_{11}\text{O}_2$ ) $^+$ ]. HRMS: found: 385.93375. Calculated for  $\text{C}_{12}\text{H}_{14}\text{O}_2\text{F}_2^{79}\text{Br}_2$ : 385.93286.

1-(4-Bromo-4,4-difluorobutyl)-3,4-dimethoxybenzene (**3c**): yield: 26%.  $^1\text{H}$  NMR: 1.94 (m, 2H); 2.36 (m, 2H); 2.65 (t,  $^3J_{\text{HH}} = 7.6$ , 2H); 3.86 (s, 3H); 3.88 (s, 3H).  $^{19}\text{F}$  NMR:  $-43.8$  (t,  $^3J_{\text{FH}} = 13.9$ , 2F). GC–MS:  $m/z$  (rel. int., ion): 310, 308 (20, 25,  $M^+$ ); 229 [7, ( $M - \text{Br}$ ) $^+$ ]; 209 [3, ( $\text{C}_{12}\text{H}_{14}\text{O}_2\text{F}$ ) $^+$ ]; 151 [100, ( $\text{C}_9\text{H}_{11}\text{O}_2$ ) $^+$ ]. HRMS: found: 308.02113. Calculated for  $\text{C}_{12}\text{H}_{15}\text{O}_2\text{F}_2^{79}\text{Br}$ : 308.02235.

2,3-Bis(2-bromo-2,2-difluoroethyl)-1,4-bis(3,4-dimethoxyphenyl)butane (**4c**): yield: 0.3 g (15%). Viscous resin.  $^1\text{H}$  NMR: 2.16–2.50 (m, 6H); 2.5–2.8 (complex AB system,  $^2J_{\text{HH}} = 14.2$ ;  $^3J_{\text{HH}} = 7.0$ , 4H); 3.76 (s, 3H); 3.80 (s, 3H); 3.85 (s, 3H); 3.86 (s, 3H); 6.52 (dd,  $^3J_{\text{HH}} = 9.2$ ;  $^3J_{\text{HH}} = 1.9$ , 1H); 6.56 (dd,  $^3J_{\text{HH}} = 8.0$ ,  $^3J_{\text{HH}} = 1.9$ , 1H); 6.70 (m, 3H); 6.79 (m, 1H).  $^{19}\text{F}$  NMR: 40.4 (m);  $-40.8$  (m);  $-41.4$  (m);  $-41.5$  (m);  $-41.9$  (m);  $-42.0$  (dt,  $^2J_{\text{FF}} = 155.95$ ;  $^3J_{\text{FH}} = 16.3$ ). MS:  $m/z$  (rel. int., ion): 618, 616, 614 (7, 14, 7,  $M^+$ ); 566 (2); 486 [2, ( $\text{C}_{23}\text{H}_{27}\text{F}_2\text{BrO}_4$ ) $^+$ ]; 349, 347 [1, 1, ( $\text{C}_{15}\text{H}_{18}\text{F}_2\text{BrO}_2$ ) $^+$ ]; 335, 333 [2, 2, ( $\text{C}_{14}\text{H}_{16}\text{F}_2\text{BrO}_2$ ) $^+$ ]; 307 (1); 290 (1); 207 (1); 189 (<1); 177 (10); 151 [100, ( $\text{C}_9\text{H}_{11}\text{O}_2$ ) $^+$ ]. Analysis: found: C, 46.7; H, 5.1; Br, 25.2; F, 11.9%. Calculated for  $\text{C}_{24}\text{H}_{28}\text{F}_4\text{Br}_2\text{O}_4$  (616.28): C, 46.7; H, 4.9; Br, 25.6; F, 12.3%. HRMS: found: 614.03015. Calculated for  $\text{C}_{24}\text{H}_{28}\text{F}_4^{79}\text{Br}_2\text{O}_4$ : 614.02904.

### 3.1.4. Addition of $\text{CF}_2\text{Br}_2$ to 4-chloroallylbenzene (**1d**)

4-Chloroallylbenzene (**1d**) (1.0 g, 6.5 mmol),  $\text{CF}_2\text{Br}_2$  (2.15 g, 10.4 mmol),  $\text{Na}_2\text{S}_2\text{O}_4$  (1.4 g, 6.5 mmol), and  $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$  (3.7 g, 9.7 mmol) were reacted at ambient temperature for 24 h and worked up as in Section 3.1.1.

1-(2,4-Dibromo-4,4-difluorobutyl)-4-chlorobenzene (**2d**): yield: 0.27 g, (11%). Colorless liquid.  $^1\text{H}$  NMR:  $\delta$ : 3.01 (complex AB system, 2H); 3.10 (dd  $^2J_{\text{HH}} = 14.6$ ;  $^3J_{\text{HH}} = 8.5$ , 1H); 3.28 (dd,  $^2J_{\text{HH}} = 14.6$ ;  $^3J_{\text{HH}} = 5.4$ , 1H); 4.36 (dq,  $^3J_{\text{HH}} = ^3J_{\text{HH}} = \text{ca. } 8.5$ ;  $^3J_{\text{HH}} = ^3J_{\text{HH}} = \text{ca. } 6.0$ , 1H); 7.17 (d,  $^3J_{\text{HH}} = 8.6$ , 2H); 7.32 (d,  $^3J_{\text{HH}} = 8.6$ , 2H).  $^{19}\text{F}$  NMR:  $-42.7$  (ddd,  $^2J_{\text{FF}} = 158.8$ ;  $^3J_{\text{FH}} = 14.5$ ;  $^3J_{\text{FH}} = 12.2$ , 1F);  $-43.4$  (ddd,  $^2J_{\text{FF}} = 158.8$ ;  $^3J_{\text{FH}} = 14.8$ ;  $^3J_{\text{FH}} = 12.1$ , 1F). MS:  $m/z$  (rel. int., ion): 364, 362, 360 (5, 7, 3,  $M^+$ ); 263, 261 [1, 1, ( $\text{C}_{10}\text{H}_8\text{ClBrF}$ ) $^+$ ]; 219, 217 [2, 1, ( $M - \text{CH}_2\text{CF}_2\text{Br}$ ) $^+$ ]; 201 [4, ( $\text{C}_{10}\text{H}_8\text{F}_2\text{Cl}$ ) $^+$ ]; 181 [6, ( $\text{C}_{10}\text{H}_7\text{FCl}$ ) $^+$ ]; 161 (1); 146 (7); 127, 125 [32, 100, ( $\text{C}_7\text{H}_6\text{Cl}$ ) $^+$ ]. Analysis: found: C, 33.5; H, 2.6; F, 10.9%. Calculated for  $\text{C}_{10}\text{H}_9\text{F}_2\text{Br}_2\text{Cl}$  (362.44): C, 33.1; H, 2.5; F, 10.5%.

1-(4-Bromo-4,4-difluorobutyl)-4-chlorobenzene (**3d**): yield: 0.31 g (17%). Colorless liquid.  $^1\text{H}$  NMR: 1.91 (m, 2H); 2.34 (m, 2H); 2.67 (t,  $^3J_{\text{HH}} = 7.6$ , 2H); 7.11 (d,  $^3J_{\text{HH}} = 8.6$ , 2H); 7.27 (d,  $^3J_{\text{HH}} = 8.6$ , 2H).  $^{19}\text{F}$  NMR:  $-43.9$  (t,  $^3J_{\text{FH}} = 13.8$ , 2F). MS:  $m/z$  (rel. int., ion): 284, 282 (16, 14,  $M^+$ ); 249 (1); 222 (1); 203 [7, ( $M - \text{Br}$ ) $^+$ ]; 183 [16, ( $\text{C}_{10}\text{H}_9\text{FCl}$ ) $^+$ ]; 161 (3); 151 (5); 146 (8); 127, 125 [32, 100, ( $\text{C}_7\text{H}_6\text{Cl}$ ) $^+$ ]. Analysis: found: C, 42.6; H, 3.5; F, 13.6%. Calculated for  $\text{C}_{10}\text{H}_{10}\text{F}_2\text{BrCl}$  (283.54): C, 42.4; H, 3.5; F, 13.4%.

2,3-Bis(2-bromo-2,2-difluoroethyl)-1,4-bis(4-chlorophenyl)butane (**4d**): yield: 0.42g (11%). Viscous resin.  $^1\text{H}$  NMR: 2.27 (m, 4H); 2.48 (m, 4H); 2.69 (complex AB system,  $^2J_{\text{HH}} = 14.1$ ;  $^3J_{\text{HH}} = 7.0$ , 2H); 6.90 (d,  $^3J_{\text{HH}} = 8.4$ , 2H); 7.04 (d,  $^3J_{\text{HH}} = 8.4$ , 2H); 7.20 (d,  $^3J_{\text{HH}} = 8.4$ , 2H); 7.30 (d,  $^3J_{\text{HH}} = 8.4$ , 2H).  $^{19}\text{F}$  NMR:  $-40.4$  (ddd,  $^2J_{\text{FF}} = 157.3$ ;  $^3J_{\text{FH}} = 16.2$ ;  $^3J_{\text{FH}} =$

10.8, 1F);  $-41.3$  (dt,  $^2J_{\text{FF}} = 157.3$ ;  $^3J_{\text{FH}} = 15.3$ , 1F);  $-41.7$  (dt,  $^2J_{\text{FF}} = 157.3$ ;  $^3J_{\text{FH}} = 14.8$ , 1F);  $-42.0$  (dt,  $^2J_{\text{FF}} = 157.3$ ;  $^3J_{\text{FH}} = 14.8$ , 1F). MS:  $m/z$  (rel. int., ion): 566, 564, 562 (6, 7, 3,  $M^+$ ); 323, 321 [<1, <1, ( $\text{C}_{13}\text{H}_{13}\text{F}_2\text{BrCl}$ ) $^+$ ]; 203, 201 [1, 2, ( $\text{C}_{10}\text{H}_8\text{F}_2\text{Cl}$ ) $^+$ ]; 181 (1); 151 (3); 127, 125 [33, 100, ( $\text{C}_7\text{H}_6\text{Cl}$ ) $^+$ ]. Analysis: found: C, 42.9; H, 3.2; F, 13.0%. Calculated for  $\text{C}_{20}\text{H}_{18}\text{F}_4\text{Br}_2\text{Cl}_2$ : (565.07): C, 42.5; H, 3.2; F, 13.4%. HRMS: found: 561.90795; Calculated for  $\text{C}_{20}\text{H}_{18}\text{F}_4^{79}\text{Br}_2^{35}\text{Cl}_2$ : 561.90884.

## 3.2. Dehydrohalogenation of adducts **2** and in situ reactions of intermediate dienes **5** with dienophiles

### 3.2.1. Dehydrohalogenation of mixtures of **2**, **3**, and **4** followed by reactions with 4-phenyl-3H-1,2,4-triazoline-3,5-dione (**6**)

Allylbenzene **1a**, **1b** or **1c** (10 mmol),  $\text{CF}_2\text{Br}_2$  (2.7 g, 13 mmol),  $\text{Na}_2\text{S}_2\text{O}_4$  (2.1 g, 10 mmol), and  $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$  (3.7 g, 9.7 mmol) were reacted at ambient temperature for 3 h and worked up as in Section 3.1.1. The crude mixture of compounds **2**, **3** and **4**, obtained after evaporation of the solvents, was re-dissolved in diethyl ether and stirred with added DBU (4.56 g, 30 mmol) at ambient temperature for 20 min, then an excess of the base was removed by washing with hydrochloric acid (5%,  $2 \times 30$  ml) followed by brine (10 ml) The organic phase was dried over  $\text{MgSO}_4$  and evaporated to ca. 3–5 ml capacity. This residue, containing dienes **5** and unchanged **3** and **4**, was dissolved in  $\text{CH}_2\text{Cl}_2$  (30 ml) and, while stirring, 4-phenyl-3H-1,2,4-triazoline-3,5-dione (**6**) (0.81 g, 46 mmol) was added portion-wise (after each addition initial purple colour of **6** quickly disappeared). The stirring was continued for 40 min, the solvents were removed on a rotary evaporator and the residue was crystallized from hexane–ethyl acetate (3:2) to give cycloadducts **7a**, **7b** and **7c** as white solids.

5,5-Difluoro-2,8-diphenyl-5,8-dihydro-[1,2,4]triazolo[1,2- $\alpha$ ]pyridazine-1,3-dione (**7a**): yield: 0.3 g (9%). Mp 183–184 °C (lit. 184–187 °C [2]).  $^1\text{H}$  NMR: 5.95 (t,  $^3J_{\text{HH}} = J_{\text{HF}} = 4.8$ , 1H); 6.43 (ddm,  $^3J_{\text{HH}} = 10.2$ ,  $^3J_{\text{HF}} = 6.2$ , 1H); 6.80 (dd,  $^3J_{\text{HH}} = 10.2$ ,  $^3J_{\text{HH}} = 4.8$ , 1H); 7.40–7.45 (m, 5H); 7.46–7.52 (m, 5H).  $^{19}\text{F}$  NMR:  $-73.5$  (ddd,  $^2J_{\text{FF}} = 220.7$ ,  $^3J_{\text{FH}} = 4.8$  Hz,  $^4J_{\text{FH}} = 0.96$ , 1F);  $-82.5$  (ddd,  $^2J_{\text{FF}} = 220.7$ ,  $^3J_{\text{FH}} = 6.2$ ,  $^4J_{\text{FH}} = 1.44$ , 1F). MS:  $m/z$  (rel. int., ion): 341 (46,  $M^+$ ); 264 [5, ( $M - \text{Ph}$ ) $^+$ ]; 166 [100, ( $\text{C}_{10}\text{H}_8\text{F}_2$ ) $^+$ ]; 146 [46, ( $\text{C}_{10}\text{H}_7\text{F}$ ) $^+$ ]; 115 [17, ( $\text{C}_9\text{H}_7$ ) $^+$ ]. Analysis: found: C, 62.9; H, 4.0; F, 10.8; N, 11.9%. Calculated for  $\text{C}_{18}\text{H}_{13}\text{F}_2\text{O}_2\text{N}_3$  (341.31): C, 63.3; H, 3.8; F, 11.1; N, 12.3%.

Analogical reaction sequence starting from isolated **2a** (5.5 mmol) gave cycloadduct **7a** in a 44% yield.

5,5-Difluoro-2-phenyl-8-*p*-tolyl-5,8-dihydro-[1,2,4]triazolo[1,2- $\alpha$ ]pyridazine-1,3-dione (**7b**): yield: 0.48 g (9%). Mp 159–160 °C.  $^1\text{H}$  NMR (in  $\text{C}_2\text{D}_6\text{CO}$ ): 2.35 (s, 3H); 5.70 (t,  $^3J_{\text{HH}} = J_{\text{HF}} = 4.7$ , 1H); 6.21 (ddm,  $^3J_{\text{HH}} = 10.3$ ,  $^3J_{\text{HF}} = 6.0$ , 1H); 6.47 (dd,  $^3J_{\text{HH}} = 10.3$ ,  $^3J_{\text{HH}} = 4.8$ , 1H); 7.20 (d,  $^3J_{\text{HH}} = 8.0$ , 2H); 7.33 (d,  $^3J_{\text{HH}} = 8.0$ , 2H); 7.35–7.46 (m, 5H).  $^{19}\text{F}$  NMR:  $-77.6$  (dd,  $^2J_{\text{FF}} = 220.1$ ,  $^3J_{\text{FH}} = 4.7$ , 1F);  $-87.6$  (ddd,  $^2J_{\text{FF}} = 220.1$ ,  $^3J_{\text{FH}} = 6.0$ ,  $^4J_{\text{FH}} = 1.0$ , 1F). MS:  $m/z$  (rel. int., ion): 355 (60,  $M^+$ ); 335 [5, ( $M - \text{HF}$ ) $^+$ ]; 264 [4, ( $M - \text{NPh}$ ) $^+$ ]; 236 [1,

( $C_{12}H_{10}ON_2F_2$ )<sup>+</sup>; 180 [100, ( $C_{11}H_{10}F_2$ )<sup>+</sup>]; 165 [29, ( $C_{10}H_7F_2$ )<sup>+</sup>]. Analysis: found: C, 64.0; H, 4.2; F, 10.3; N, 11.4%. Calculated for  $C_{19}H_{15}F_2O_2N_3$  (355.34): C, 64.2; H, 4.2; F, 10.7; N, 11.8%. HRMS: found: 355.11258. Calculated for  $C_{19}H_{15}F_2O_2N_3$ : 355.11323.

8-(3,4-Dimethoxyphenyl)-5,5-difluoro-2-phenyl-5,8-dihydro-[1,2,4]triazolo[1,2- $\alpha$ ]pyridazine-1,3-dione (**7c**): yield: 0.21 g (9%). Mp 132 °C (lit. 130–134 [2]). <sup>1</sup>H NMR (in  $C_2D_6CO$ ): 3.78 (s, 3H); 3.80 (s, 3H); 5.87 (t, <sup>3</sup> $J_{HH} = J_{HF} = 4.8$ , 1H); 6.40 (ddm, <sup>3</sup> $J_{HH} = 10.2$ , <sup>3</sup> $J_{HF} = 6.2$ , 1H); 6.77 (dd, <sup>3</sup> $J_{HH} = 10.2$ , <sup>3</sup> $J_{HH} = 4.8$ , 1H); 6.98 (m, 2H); 7.05 (s, 1H); 7.39–7.56 (m, 5H). <sup>19</sup>F NMR: –73.2 (ddd, <sup>2</sup> $J_{FF} = 220.8$ , <sup>3</sup> $J_{FH} = 4.9$ , <sup>4</sup> $J_{FH} = 1.05$ , 1F); –82.4 (ddd, <sup>2</sup> $J_{FF} = 220.8$ , <sup>3</sup> $J_{FH} = 6.3$  Hz, <sup>4</sup> $J_{FH} = 1.05$ , 1F). MS: *m/z* (rel. int., ion): 401 (100,  $M^+$ ); 370 [2, ( $M - OCH_3$ )<sup>+</sup>]; 309 (6); 264 (9); 226 [66, ( $C_{12}H_{12}O_2F_2$ )<sup>+</sup>]; 195 [15, ( $C_{11}H_9OF_2$ )<sup>+</sup>]; 151 [10, ( $C_9H_{11}O_2$ )<sup>+</sup>]. Analysis: found: C, 59.4; H, 4.7; F, 9.1; N, 10.4%. Calculated for  $C_{20}H_{17}F_2O_4N_3$  (401.34): C, 59.8; H, 4.3; F, 9.5; N, 10.5%. HRMS: found: 401.11991. Calculated for  $C_{20}H_{17}F_2O_4N_3$ : 401.11871.

### 3.2.2. Dehydrohalogenation of pure **2a** followed by the reaction with diethyl azodicarboxylate (**8**)

Compound **2a** (0.3 g, 0.92 mmol) was dissolved in  $CH_2Cl_2$  (10 ml) and treated with DBU (0.42 g, 2.7 mmol) at room temperature for 20 min. After work up as described in Section 3.2.1, the resultant oil was dissolved in dry  $CH_2Cl_2$ , diethyl azodicarboxylate (0.32 g, 1.6 mmol), and  $ZnCl_2$  (20 mg) were added and the reaction mixture was stirred at ambient temperature for 3 days under the argon atmosphere. An orange colored oil obtained after removal of the solvent was purified by column chromatography (silica gel, hexanes/ $AcOEt$  1:1) to give **9** as a colorless oil. Yield 0.1 g (32%).

Diethyl 3,3-difluoro-6-phenyl-3,6-dihydro-pyridazine-1,2-dicarboxylate (**9**): <sup>1</sup>H NMR: 1.06 (m, 3H); 1.28 (m, 3H); 4.05 (m, 2H); 4.27 (m, 2H); 5.99 (m, 1H); 6.08 (dd, <sup>3</sup> $J_{HH} = 9.0$ , <sup>3</sup> $J_{HF} = 6.8$ , 1H); 6.60 (dd, <sup>3</sup> $J_{HH} = 9.0$ , <sup>3</sup> $J_{HH} = 4.9$ , 1H); 7.35 (m, 5H). <sup>19</sup>F NMR: –72.1 (m, 1F); –72.7 (m, 1F). MS: *m/z* (rel. int., ion): 340 (3,  $M^+$ ); 320 [ $<1$ , ( $M - HF$ )<sup>+</sup>]; 296 [3, ( $M - CO_2$ )<sup>+</sup>]; 269, 268 [12, 81, ( $M - HCO_2Et$ )<sup>+</sup>]; 253 [6, ( $M - NCO_2Et$ )<sup>+</sup>]; 248 [5, ( $C_{12}H_6F_2N_2O_2$ )<sup>+</sup>]; 223 [8, ( $C_{12}H_{13}F_2N_2$ )<sup>+</sup>]; 195 [28, ( $M - 2CO_2Et$ )<sup>+</sup>]; 180 [19, ( $C_{10}H_8F_2N$ )<sup>+</sup>]; 175 [81, ( $C_{12}H_{12}F$ )<sup>+</sup>]; 166 [100, ( $C_{10}H_8F_2$ )<sup>+</sup>]; 146 [40, ( $C_{10}H_7F$ )<sup>+</sup>]; 127 [12, ( $C_{10}H_7$ )<sup>+</sup>]; 115 (20); 99 (38); 91 (9). HRMS: found: 340.12284. Calculated for  $C_{16}H_{18}O_4N_2F_2$ : 340.12346.

### 3.3. Addition of $CF_3I$ to allylbenzenes and reactions of the adducts

#### 3.3.1. Addition of $CF_3I$ to allylbenzene (**1a**)

A pressure glass ampoule (150 ml) fitted with a Rotaflo<sup>®</sup> valve and magnetic stirring bar was filled with a water-acetonitrile solution (1:1, 40 ml), sodium dithionite (1.8 g, 8.5 mmol [85%]),  $Na_3PO_4 \cdot 12H_2O$  (6.5 g, 17 mmol) and allylbenzene (**1a**) (1.0 g, 8.5 mmol). The ampoule was cooled to –78 °C (dry ice/acetone), evacuated, then trifluoroiodomethane (2.5 g, 13 mmol) was condensed in it. After warming up to ambient temperature the contents of the ampoule was

stirred for 6 h, then water was added (20 ml), the reaction mixture was extracted with diethyl ether (3 × 50 ml) and the combined extract were dried over  $MgSO_4$ . The crude product obtained after evaporation of the solvent was subjected to column chromatography (hexanes) to give (4,4,4-trifluoro-2-iodobutyl)benzene (**10a**) as colorless liquid. Yield: 1.51 g (57%). <sup>1</sup>H NMR: 2.81 (dq, <sup>2</sup> $J_{HH} = 15.7$ ; <sup>3</sup> $J_{HF} = 10.0$ ; <sup>3</sup> $J_{HH} = 6.5$ , 1H); 2.87 (dq, <sup>2</sup> $J_{HH} = 15.7$ ; <sup>3</sup> $J_{HF} = 10.0$ ; <sup>3</sup> $J_{HH} = 7.0$ , 1H); 2.20 (dd, <sup>2</sup> $J_{HH} = 14.5$ ; <sup>3</sup> $J_{HH} = 8.3$ , 1H); 3.25 (dd, <sup>2</sup> $J_{HH} = 14.5$ ; <sup>3</sup> $J_{HH} = 6.5$ , 1H); 4.33 (dq, <sup>3</sup> $J_{HH} = 8.2$ ; <sup>3</sup> $J_{HH} = 6.7$ , 1H); 7.19 (m, 2H); 7.32 (m, 3H). <sup>19</sup>F NMR: –64.1 (t, <sup>3</sup> $J_{HF} = 10.0$ , 3F). MS: *m/z* (rel. int., ion): 314 (4,  $M^+$ ); 255 [12, ( $C_{10}H_9I$ )<sup>+</sup>]; 235 (1); 215 (3); 195 (3); 187 [100, ( $M - I$ )<sup>+</sup>]; 159 (15); 147 [43, ( $C_{10}H_9F_2$ )<sup>+</sup>]; 117 [23, ( $C_9H_{10}$ )<sup>+</sup>]; 103 (11); 91 [49, ( $C_7H_7$ )<sup>+</sup>]. Analysis: found: C, 38.6; H, 3.4; F, 18.5; I, 40.8%. Calculated for  $C_{10}H_{11}F_3I$  (314.09): C, 38.2; H, 3.2; F, 18.1; I, 40.4%.

#### 3.3.2. Addition of $CF_3I$ to 3,4-dimethoxyallylbenzene (**1c**)

3,4-Dimethoxyallylbenzene (**1c**) (1.5 g, 8.4 mmol), sodium dithionite (1.8 g, 8.5 mmol [85%]),  $Na_3PO_4 \cdot 12H_2O$  (6.5 g, 17 mmol) and  $CF_3I$  (2.5 g, 13 mmol) were reacted and worked up as above. The crude product obtained after evaporation of the solvent was subjected to column chromatography (hexanes/ethanol 4:1) to give 1-(4,4,4-trifluoro-2-iodobutyl)-3,4-dimethoxybenzene (**10c**) as yellowish liquid. Yield: 2.45 g (78%). <sup>1</sup>H NMR: 2.83 (complex m, <sup>3</sup> $J_{HF} = 10.3$ , 2H); 3.17 (d, <sup>3</sup> $J_{HH} = 7.3$ , 2H); 3.88 (s, 3H); 3.89 (s, 3H); 4.31 (qn, <sup>3</sup> $J_{HH} = ca.$  7.0, 1H); 6.70 (d, <sup>4</sup> $J_{HH} = 2.0$ , 1H); 6.74 (dd, <sup>3</sup> $J_{HH} = 8.1$ ; <sup>4</sup> $J_{HH} = 2.0$ , 1H); 6.83 (d, <sup>3</sup> $J_{HH} = 8.1$ , 1H). <sup>19</sup>F NMR: –64.1 (t, <sup>3</sup> $J_{HF} = 10.3$ , 3F). MS: *m/z* (rel. int., ion): 374 (67,  $M^+$ ); 355 [ $<1$ , ( $M - F$ )<sup>+</sup>]; 315 [5, ( $C_{12}H_{12}IO_2$ )<sup>+</sup>]; 285 [1, ( $C_{11}H_{10}IO$ )<sup>+</sup>]; 247 [91, ( $M - I$ )<sup>+</sup>]; 219 (10); 207 (7); 164 [12, ( $C_{10}H_{12}O_2$ )<sup>+</sup>]; 151 [100, ( $C_9H_{11}O_2$ )<sup>+</sup>]. Analysis: found: C, 38.9; H, 3.7; F, 15.2; I, 33.6%. Calculated for  $C_{12}H_{14}F_3IO_2$  (374.14): C, 38.5; H, 3.8; F, 15.2; I, 33.9%.

#### 3.3.3. Reductive deiodination of compounds **10a** and **10c**

(4,4,4-Trifluoro-2-iodobutyl)benzene (**10a**) (1.26 g, 4 mmol) or 1-(4,4,4-trifluoro-2-iodobutyl)-3,4-dimethoxybenzene (**10c**) (2.45 g, 6.5 mmol) and zinc powder (0.9 g 13 mmol) were refluxed in ethanol (50 ml) for 10 h. After cooling to ambient temperature, brine was added, organic oil was extracted with diethyl ether (4 × 40 ml) and the combined extracts were dried over  $MgSO_4$ . The crude products obtained after removal of the solvent were purified by column chromatography (silica gel, hexanes or hexanes-ethanol 19:1, respectively) to give compounds **11a** and **11c** as colorless oils.

(4,4,4-Trifluorobutyl)benzene (**11a**): yield 0.32 g (43%). <sup>1</sup>H NMR: 1.91 (m, 2H); 2.08 (complex m, <sup>3</sup> $J_{HF} = 10.9$ , 2H); 2.69 (t, <sup>3</sup> $J_{HH} = 7.6$ , 2H); 7.21 (m, 3H); 7.31 (m, 2H). <sup>19</sup>F NMR: –66.7 (t, <sup>3</sup> $J_{HF} = 10.9$ , 3F). MS: *m/z* (rel. int., ion): 188 (18,  $M^+$ ); 149 [2, ( $C_{10}H_{10}F$ )<sup>+</sup>]; 117 [3, ( $C_9H_9$ )<sup>+</sup>]; 115 (2); 105 [2, ( $M - CF_3CH_2$ )<sup>+</sup>]; 91 [100, ( $C_7H_7$ )<sup>+</sup>]. Analysis: found: C, 63.4; H, 5.7; F, 30.1%. Calculated for  $C_{10}H_{11}F_3$  (188.19): C, 63.8; H, 5.9; F, 30.3%. HRMS: found: 188.08211. Calculated for  $C_{10}H_{11}F_3$ : 188.08129.

1-(4,4,4-Trifluorobutyl)-3,4-dimethoxybenzene (**11c**): yield: 1.18 g, (73%).  $^1\text{H}$  NMR: 1.87 (m, 2H); 2.08 (complex m,  $^3J_{\text{HF}} = 10.8$ , 2H); 2.64 (t,  $^3J_{\text{HH}} = 7.6$ , 2H); 3.86 (s, 3H); 3.88 (s, 3H); 6.70 (d,  $^4J_{\text{HH}} = 2.0$ , 1H); 6.72 (dd,  $^3J_{\text{HH}} = 8.0$ ;  $^4J_{\text{HH}} = 2.0$ , 1H); 6.80 (d,  $^3J_{\text{HH}} = 8.0$ , 1H).  $^{19}\text{F}$  NMR:  $-66.6$  (t,  $^3J_{\text{HF}} = 10.8$ , 3F). MS:  $m/z$  (rel. int., ion): 248 (43,  $M^+$ ); 233 [2, ( $M - \text{CH}_3$ ) $^+$ ]; 219 (5); 209 [1, ( $\text{C}_{12}\text{H}_{14}\text{FO}_2$ ) $^+$ ]; 165 [2, ( $M - \text{CF}_3\text{CH}_2$ ) $^+$ ]; 151 [100, ( $\text{C}_9\text{H}_{11}\text{O}_2$ ) $^+$ ]. Analysis: found: C, 57.7; H, 5.7; F, 23.2%. Calculated for  $\text{C}_{12}\text{H}_{15}\text{F}_3\text{O}_2$  (248.24): C, 58.1; H, 6.1; F, 22.9%.

### 3.3.4. Dehydroiodination of compound **10a**

(4,4,4-Trifluoro-2-iodobutyl)benzene (**10a**) (1.18 g, 3.7 mmol) and DBU (1.7 g 11 mmol) were refluxed in hexanes (50 ml) for 12 h. The base was removed by washing with hydrochloric acid (5%) followed by brine. The organic phase was dried over  $\text{MgSO}_4$ , evaporated, and the residue was subjected to column chromatography to give (4,4,4-trifluorobut-1-enyl)benzene (**12**) as colorless liquid. Yield: 0.36 g (53%).  $^1\text{H}$  NMR: 2.99 (qdd,  $^3J_{\text{HF}} = 10.7$ ;  $^3J_{\text{HH}} = 7.3$ ;  $^4J_{\text{HH}} = 1.4$ , 2H); 6.11 (dt,  $^3J_{\text{HH}} = 15.8$ ;  $^3J_{\text{HH}} = 7.3$ , 1H); 6.60 (d,  $^3J_{\text{HH}} = 15.8$ , 1H); 7.32 (m, 5H).  $^{19}\text{F}$  NMR:  $-66.7$  (t,  $^3J_{\text{HF}} = 10.7$ , 3F). MS:  $m/z$  (rel. int., ion): 186 (100,  $M^+$ ); 165 (14); 147 [8, ( $\text{C}_{10}\text{H}_8\text{F}^+$ ); 117 [69, ( $M - \text{CF}_3$ ) $^+$ ]; 91 [16, ( $\text{C}_7\text{H}_7$ ) $^+$ ]; 69 (9). Analysis: found: C, 64.9; H, 4.9; F, 30.3%. Calculated for  $\text{C}_{10}\text{H}_9\text{F}_3$  (186.17): C, 64.5; H, 4.9; F, 30.6%.

## 3.4. Addition of $(\text{CF}_3)_2\text{CFI}$ to allylbenzenes and reactions of the adducts

### 3.4.1. Addition of $(\text{CF}_3)_2\text{CFI}$ to allylbenzenes

Sodium dithionite (2.1 g, 10 mmol [85%]), sodium hydrogen carbonate (1.68 g, 20 mmol), allylbenzene **1a–f** (10 mol) and 2-iodo-heptafluoropropane (4.14 g, 14 mol) were added to a water–acetonitrile solution (1:1, 40 ml) and the reaction mixture was vigorously stirred at ambient temperature for 2 h ( $\text{CO}_2$  evolution occurred). After completion of the reaction water (20 ml) was added, the reaction mixture was extracted with diethyl ether (3  $\times$  50 ml) and the combined extracts were dried over  $\text{MgSO}_4$ . The crude mixtures of products obtained after removal of the solvent was subjected to column chromatography (silica gel, hexanes:ethanol, 19:1) to give compounds **13** as colorless liquids.

(4,5,5,5-Tetrafluoro-2-iodo-4-trifluoromethylpentyl)benzene (**13a**): yield: 3.27 g (79%).  $^1\text{H}$  NMR: 2.84–3.01 (complex AB systems,  $^2J_{\text{HH}} = 16.4$ , 2H); 3.13 (dd,  $^2J_{\text{HH}} = 14.6$ ,  $^3J_{\text{HH}} = 9.2$ , 1H); 3.28 (dd,  $^2J_{\text{HH}} = 14.6$ ,  $^3J_{\text{HH}} = 5.4$ , 1H); 4.44 (m, 1H, *CHI*); 7.18 (m, 2H); 7.32 (m, 3H).  $^{19}\text{F}$  NMR:  $-76.7$  (qn,  $^4J_{\text{FF}} = 8.7$ , 3F);  $-77.7$  (qn,  $^4J_{\text{FF}} = 8.7$  Hz, 3F);  $-185.9$  (complex m, 1F). MS:  $m/z$  (rel. int., ion): 414 (3,  $M^+$ ); 287 [100, ( $M - \text{I}$ ) $^+$ ]; 268 [1, ( $\text{C}_{12}\text{H}_{10}\text{F}_6$ ) $^+$ ]; 247 (1); 189 (4); 127 (9); 117 [31, ( $\text{C}_9\text{H}_9$ ) $^+$ ]; 91 [87, ( $\text{C}_7\text{H}_7$ ) $^+$ ]. Analysis: found: C, 35.1, H, 2.6, F, 32.5, I, 30.2%. Calculated for  $\text{C}_{12}\text{H}_{10}\text{F}_7\text{I}$  (414.10): C, 34.8, H, 2.4; F, 32.1, I, 30.6%.

1-Methyl-4-(4,5,5,5-tetrafluoro-2-iodo-4-trifluoromethylpentyl)benzene (**13b**): yield: 2.52 g (65%).  $^1\text{H}$  NMR: 2.33 (s, 3H); 2.83–3.02 (complex AB systems,  $^2J_{\text{HH}} = 16.4$  Hz, 2H);

3.11 (dd,  $^2J_{\text{HH}} = 14.6$ ;  $^3J_{\text{HH}} = 9.1$ , 1H); 3.23 (dd,  $^2J_{\text{HH}} = 14.6$ ;  $^3J_{\text{HH}} = 5.4$ , 1H); 4.42 (m, 1H); 7.06 (d,  $^3J_{\text{HH}} = 8.2$ , 2H); 7.14 (d,  $^3J_{\text{HH}} = 8.2$ , 2H).  $^{19}\text{F}$  NMR:  $-76.7$  (qn,  $^4J_{\text{FF}} = 9.0$ , 3F);  $-77.7$  (dq,  $^4J_{\text{FF}} = 9.0$ ,  $^3J_{\text{FF}} = 2.1$ , 3F);  $-185.8$  (complex m, 1F). MS:  $m/z$  (rel. int., ion): 428 (7,  $M^+$ ); 409 [1, ( $M - \text{F}$ ) $^+$ ]; 301 [100, ( $M - \text{I}$ ) $^+$ ]; 282 [1, ( $\text{C}_{13}\text{H}_{12}\text{F}_6$ ) $^+$ ]; 261 (<1); 209 (1); 182 (5); 145 (2); 131 (13); 117 (16); 105 [56, ( $\text{C}_8\text{H}_6$ ) $^+$ ]; 91 [13, ( $\text{C}_7\text{H}_7$ ) $^+$ ]. Analysis: found: C, 36.8; H, 2.8; F, 31.5; I, 29.3%. Calculated for  $\text{C}_{13}\text{H}_{12}\text{F}_7\text{I}$  (428.13): C, 36.5, H, 2.8; F, 31.1; I, 29.6%.

1-Methoxy-4-(4,5,5,5-tetrafluoro-2-iodo-4-trifluoromethylpentyl)benzene (**13e**): yield: 4.0 g (90%).  $^1\text{H}$  NMR: 2.83–2.99 (complex AB systems,  $^2J_{\text{HH}} = 16.3$ , 2H); 3.09 (dd,  $^2J_{\text{HH}} = 14.7$ ,  $^3J_{\text{HH}} = 8.9$  Hz, 1H); 3.20 (dd,  $^2J_{\text{HH}} = 14.7$ ,  $^3J_{\text{HH}} = 5.6$ , 1H); 4.40 (m, 1H); 6.86 (d,  $^3J_{\text{HH}} = 8.8$ , 2H); 7.10 (d,  $^3J_{\text{HH}} = 8.8$ , 2H).  $^{19}\text{F}$  NMR:  $-76.8$  (qn,  $^4J_{\text{FF}} = 9.0$ , 3F);  $-77.7$  (dq complex,  $^4J_{\text{FF}} = 9.0$ ,  $^3J_{\text{FF}} = 2.1$ , 3F);  $-185.8$  (complex m, 1F). MS:  $m/z$  (rel. int., ion): 444 (24,  $M^+$ ); 425 [2, ( $M - \text{F}$ ) $^+$ ]; 317 [100, ( $M - \text{I}$ ) $^+$ ]; 298 (3); 147 [17, ( $\text{C}_{10}\text{H}_{11}\text{O}$ ) $^+$ ]; 134 [18, ( $\text{C}_9\text{H}_{10}\text{O}$ ) $^+$ ]; 121 [67, ( $\text{C}_8\text{H}_9\text{O}$ ) $^+$ ]. Analysis: found: C, 35.2; H, 2.6, F, 30.1%. Calculated for  $\text{C}_{13}\text{H}_{12}\text{F}_7\text{OI}$  (444.13): C, 35.2; H, 2.7, F, 29.9%.

1-Bromo-4-(4,5,5,5-tetrafluoro-2-iodo-4-trifluoromethylpentyl)benzene (**13f**): yield: 0.73 g (42%).  $^1\text{H}$  NMR: 2.8–3.0 (complex AB systems,  $^2J_{\text{HH}} = 16.3$ , 2H); 3.05 (dd,  $^2J_{\text{HH}} = 14.7$ ,  $^3J_{\text{HH}} = 9.6$ , 1H); 3.26 (dd,  $^2J_{\text{HH}} = 14.7$ ,  $^3J_{\text{HH}} = 4.7$  Hz, 1H); 4.40 (m, 1H); 7.06 (d,  $^3J_{\text{HH}} = 8.4$ , 2H); 7.46 (d,  $^3J_{\text{HH}} = 8.4$ , 2H).  $^{19}\text{F}$  NMR:  $-76.4$  (qn,  $^4J_{\text{FF}} = 8.7$ , 3F);  $-77.8$  (dq,  $^4J_{\text{FF}} = 9.4$ ,  $^3J_{\text{FF}} = 2.0$ , 3F);  $-185.6$  (complex m, 1F). MS:  $m/z$  (rel. int., ion): 494, 492 (15, 16,  $M^+$ ); 367, 365 [98, 100, ( $M - \text{I}$ ) $^+$ ]; 286 [25, ( $\text{C}_{12}\text{H}_9\text{F}_7$ ) $^+$ ]; 169, 171 [14, 14, ( $\text{C}_7\text{H}_6\text{Br}$ ) $^+$ ]; 117 (21). Analysis: found: C, 29.4; H, 1.8; F, 27.0%. Calculated for  $\text{C}_{12}\text{H}_9\text{F}_7\text{IBr}$  (493.00): C, 29.2; H, 1.8; F, 27.0%.

### 3.4.2. Reductive deiodination of compound **13a**

(4,5,5,5-Tetrafluoro-2-iodo-4-trifluoromethylpentyl)benzene (**13a**) (2.5 g, 6 mmol) and zinc powder (0.9 g 13 mmol) were refluxed in ethanol (50 ml) for 10 h and worked up as in Section 3.3.3 to give (4,5,5,5-tetrafluoro-4-trifluoromethylpentyl)benzene (**14a**). Colorless liquid. Yield: 0.8 g (46%).  $^1\text{H}$  NMR: 1.91 (m, 2H); 2.09 (m, 2H); 2.68 (t,  $^3J_{\text{HH}} = 7.5$ , 2H); 7.18 (dm,  $^3J_{\text{HH}} = 7.5$ ,  $^4J_{\text{HH}} = 0.6$ , 2H); 7.22 (tm,  $^3J_{\text{HH}} = \text{ca. } 7.3$ , 1H); 7.31 (m, 2H).  $^{19}\text{F}$  NMR:  $-76.8$  (d,  $^3J_{\text{FF}} = 6.05$ , 6F);  $-184.2$  (m,  $^3J_{\text{FF}} = 6.05$ , 1F). MS:  $m/z$  (rel. int., ion): 288 (8,  $M^+$ ); 266 [52, ( $\text{C}_{12}\text{H}_8\text{F}_6$ ) $^+$ ]; 259 (19); 197 [44, ( $\text{C}_{11}\text{H}_8\text{F}_3$ ) $^+$ ]; 177 [100, ( $\text{C}_{11}\text{H}_7\text{F}_2$ ) $^+$ ]; 128 [36, ( $\text{C}_{10}\text{H}_8$ ) $^+$ ]; 91 [70, ( $\text{C}_7\text{H}_7$ ) $^+$ ]. Analysis: found: C, 50.1; H, 3.8; F, 46.4%. Calculated for  $\text{C}_{12}\text{H}_{11}\text{F}_7$  (288.21): C, 50.0; H, 3.8; F, 46.1%. HRMS: found: 288.07528. Calculated for  $\text{C}_{12}\text{H}_{11}\text{F}_7$ : 288.07490.

### 3.4.3. Dehydrohalogenation of compounds **13**: preparation of bis(trifluoromethyl)dienes (**15**)

Compound **13** (6.2 mmol) was dissolved in hexanes (60 ml) then DBU (2.82 g, 18.5 mmol) was added (immediately a white precipitate was formed) and the reaction mixture was refluxed for 12 h. An excess of the base was removed by washing with hydrochloric acid (5%, 2  $\times$  40 ml) followed by brine (40 ml) and the organic phase was dried over  $\text{MgSO}_4$ . The residue

obtained after removal of the solvent was subjected to column chromatography (silica gel, hexanes/ethanol 19:1) to give dienes **15**.

(5,5,5-Trifluoro-4-trifluoromethylpenta-1,3-dienyl)benzene (**15a**): yield: 1.38 g (84%). Colorless liquid.  $^1\text{H}$  NMR ( $\text{C}_2\text{D}_6\text{CO}$ ): 7.27 (ddq,  $^3J_{\text{HH}} = 15.3$ ,  $^3J_{\text{HH}} = 11.7$ ,  $^5J_{\text{HF}} = 1.0$ , 1H); 7.45 (m, 3H); 7.46 (d, overlapped by Ph signal,  $^3J_{\text{HH}} = \text{ca. } 15$  Hz, 1H); 7.59 (dm,  $^3J_{\text{HH}} = \text{ca. } 11.6$  Hz, 1H); 7.68 (m, 2H).  $^{19}\text{F}$  NMR ( $\text{C}_2\text{D}_6\text{CO}$ ):  $-57.2$  (qdd,  $^4J_{\text{FF}} = 6.8$ ,  $^4J_{\text{HF}} = 2.0$ ,  $^5J_{\text{HF}} = 1.0$ , 3F);  $-62.7$  (qdd,  $^4J_{\text{FF}} = 6.8$ ,  $^4J_{\text{HF}} = 2.0$ ,  $^5J_{\text{HF}} = 1.0$ , 3F). MS:  $m/z$  (rel. int., ion): 266 (62,  $M^+$ ); 247 [12, ( $M - \text{F}$ ) $^+$ ]; 227 [7, ( $\text{C}_{12}\text{H}_7\text{F}_5$ ) $^+$ ]; 197 [48, ( $M - \text{CF}_3$ ) $^+$ ]; 177 [100, ( $M - \text{HF}, \text{CF}_3$ ) $^+$ ]; 164 (2); 151 (5); 146 (9); 128 [38, ( $M - 2\text{CF}_3$ ) $^+$ ]; 115 (9); 91 (18). Analysis: found: C, 54.1; H, 3.1; F, 42.7%. Calculated for  $\text{C}_{12}\text{H}_8\text{F}_6$  (266.18): C, 54.1; H, 3.0; F, 42.8%.

1-Methyl-4-(5,5,5-trifluoro-4-trifluoromethylpenta-1,3-dienyl)benzene (**15b**): yield: 1.14 g (81%). Colorless liquid.  $^1\text{H}$  NMR ( $\text{C}_2\text{D}_6\text{CO}$ ): 2.37 (s, 3H); 7.21 (ddq,  $^3J_{\text{HH}} = 15.2$ ,  $^3J_{\text{HH}} = 11.8$ ,  $^5J_{\text{HF}} = 1.0$ , 1H); 7.28 (d,  $^3J_{\text{HH}} = 8.0$ , 2H); 7.43 (d,  $^3J_{\text{HH}} = 15.2$ , 1H); 7.55 (overlapped by Ph signal, 1H); 7.57 (d,  $^3J_{\text{HH}} = 8.0$ , 2H).  $^{19}\text{F}$  NMR ( $\text{C}_2\text{D}_6\text{CO}$ ):  $-57.2$  (qd,  $^4J_{\text{FF}} = 6.8$ ,  $^5J_{\text{HF}} = 1.0$ , 3F);  $-62.7$  (qd,  $^4J_{\text{FF}} = 6.8$ ,  $^5J_{\text{HF}} = 1.0$ , 3F). MS:  $m/z$  (rel. int., ion): 280 (100,  $M^+$ ); 261 [14, ( $M - \text{F}$ ) $^+$ ]; 245 [8, ( $\text{C}_{12}\text{H}_6\text{F}_5$ ) $^+$ ]; 211 [40, ( $M - \text{CF}_3$ ) $^+$ ]; 191 [33, ( $\text{C}_{12}\text{H}_9\text{F}_2$ ) $^+$ ]; 182 (4); 142 [8, ( $\text{C}_{11}\text{H}_{10}$ ) $^+$ ]; 115 (3); 105 (4); 91 (3); 69 (3). Analysis: found: C, 55.4; H, 3.5; F 40.4%. Calculated for  $\text{C}_{13}\text{H}_{10}\text{F}_6$  (280.21): C, 55.7; H, 3.6; F, 40.7%.

1-Methoxy-4-(5,5,5-trifluoro-4-trifluoromethylpenta-1,3-dienyl)benzene (**15e**): yield: 2.16 g (82%). White solid. Mp 53–55 °C.  $^1\text{H}$  NMR: 3.84 (s, 3H); 6.92 (d,  $^3J_{\text{HH}} = 8.8$  Hz, 2H); 7.01 (dm,  $^3J_{\text{HH}} = \text{ca. } 11.3$ , 2H); 7.16 (dd,  $^3J_{\text{HH}} = 11.3$ ,  $^4J_{\text{HF}} = 1.1$ , 1H); 7.47 (d,  $^3J_{\text{HH}} = 8.8$ , 2H).  $^{19}\text{F}$  NMR:  $-58.0$  (q,  $^4J_{\text{FF}} = 6.8$ , 3F);  $-63.5$  (q,  $^4J_{\text{FF}} = 6.8$ , 3F). MS:  $m/z$  (rel. int., ion): 296 (100,  $M^+$ ); 277 [18, ( $M - \text{F}$ ) $^+$ ]; 227 [82, ( $M - \text{CF}_3$ ) $^+$ ]; 212 [29, ( $\text{C}_{10}\text{H}_5\text{F}_6$ ) $^+$ ]; 207 [50, ( $\text{C}_{11}\text{H}_7\text{F}_2$ ) $^+$ ]; 195 (9); 183 (10); 164 (31); 158 [30, ( $\text{C}_{10}\text{H}_8$ ) $^+$ ]; 145 (12); 133 (13); 115 (30); 69 (16). Analysis: found: C, 52.3; H, 3.2; F, 38.8%. Calculated for  $\text{C}_{13}\text{H}_{10}\text{F}_6\text{O}$  (296.21): C, 52.7; H, 3.4; F, 38.5%.

1-Bromo-4-(5,5,5-trifluoro-4-trifluoromethylpenta-1,3-dienyl)benzene (**15f**): yield: 0.33 g (82%). Colorless liquid.  $^1\text{H}$  NMR ( $\text{C}_2\text{D}_6\text{CO}$ ): 7.30 (ddq,  $^3J_{\text{HH}} = 15.3$ ,  $^3J_{\text{HH}} = 11.6$ ,  $^5J_{\text{HF}} = 1.0$ , 1H); 7.45 (d,  $^3J_{\text{HH}} = 15.3$ , 1H); 7.59 (dd,  $^3J_{\text{HH}} = 11.6$ ,  $^4J_{\text{HF}} = 0.6$ , 1H); 7.64 (m, 4H).  $^{19}\text{F}$  NMR ( $\text{C}_2\text{D}_6\text{CO}$ ):  $-57.2$  (q,  $^4J_{\text{FF}} = 6.8$ , 3F);  $-62.8$  (q,  $^4J_{\text{FF}} = 6.8$ , 3F). MS:  $m/z$  (rel. int., ion): 346, 344 (47, 47,  $M^+$ ); 325 (4); 265 [3, ( $M - \text{Br}$ ) $^+$ ]; 245 [58, ( $M - \text{Br}, \text{HF}$ ) $^+$ ]; 196 [100, ( $M - \text{Br}, \text{CF}_3$ ) $^+$ ]; 177 (7); 146 (10). Analysis: found: C, 41.6; H, 2.1; Br, 23.2; F, 33.2%. Calculated for  $\text{C}_{12}\text{H}_7\text{F}_6\text{Br}$  (345.08): C, 41.8; H, 2.0; Br, 23.2; F, 33.0%.

#### 3.4.4. Reaction of diene **15a** with 4-phenyl-3H-1,2,4-triazoline-3,5-dione (**6**)

(5,5,5-Trifluoro-4-trifluoromethylpenta-1,3-dienyl)benzene (**15a**) (0.4 g, 1.5 mmol), 4-phenyl-3H-1,2,4-triazoline-3,5-dione (**6**) (0.28 g, 1.6 mmol) and MeCN (10 ml) were heated in a pressure glass ampoule at 80 °C for 96 h. GC–MS analysis

of the reaction mixture exhibited the presence of 12% of cycloadduct, 2,8-diphenyl-5,5-bis(trifluoromethyl)-5,8-dihydro-[1,2,4]-triazolo[1,2- $\alpha$ ]pyridazine-1,3-dione (**16**). GC–MS:  $m/z$  (rel. int., ion): 441 (100,  $M^+$ ); 422 [4, ( $M - \text{F}$ ) $^+$ ]; 372 [2, ( $M - \text{CF}_3$ ) $^+$ ]; 294 [7, ( $M - \text{PhC}_2\text{O}_2\text{N}$ ) $^+$ ]; 280 [ $<1$ , ( $\text{C}_{12}\text{H}_8\text{F}_6\text{N}$ ) $^+$ ]; 225 [50, ( $\text{C}_{11}\text{H}_8\text{F}_3\text{N}_2$ ) $^+$ ]; 197 [25, ( $\text{C}_{11}\text{H}_8\text{F}_3$ ) $^+$ ]; 177 [27, ( $\text{C}_{11}\text{H}_7\text{F}_2$ ) $^+$ ]; 132 [50, ( $\text{C}_{10}\text{H}_{12}$ ) $^+$ ]; 91 [21, ( $\text{C}_7\text{H}_7$ ) $^+$ ].

#### 3.5. Addition of $(\text{CF}_3)_2\text{CFI}$ to allylpyridines **17** followed by dehydrohalogenation: preparation of bis(trifluoromethyl)dienes (**19**)

Allylpyridine **17a** or **17b** (0.29 g, 2.1 mmol or 1.03 g, 8.6 mmol),  $\text{Na}_2\text{S}_2\text{O}_4$  (0.45 g, 2.1 mmol or 1.8 g, 8.7 mmol), and  $\text{NaHCO}_3$  (0.33 g, 4 mmol or 1.68 g, 20 mmol) were suspended in water–acetonitrile solution (1:1, 10 or 40 ml, respectively), the suspension was cooled to 0 °C then  $(\text{CF}_3)_2\text{CFI}$  (0.68 g, 2.3 mmol or 2.96 g, 10 mmol) was added. The reaction mixture was stirred at 0 °C for 0.5 h followed by 1 h at ambient temperature. Organic products were extracted with diethyl ether ( $3 \times 30$  ml), the combined extracts were dried over  $\text{MgSO}_4$  and evaporated. The yellowish residue was dissolved in hexanes, DBU was added (0.95 g, 6.3 mmol or 2.84 g, 18 mmol) and the solution was left at ambient temperature for 12 h. The residue obtained after removal of the solvent was subjected to column chromatography (silica gel, hexanes/ethyl acetate 3:2) to give dienes **19a** and **19b** as yellowish solids.

2-(5,5,5-Trifluoro-4-trifluoromethylpenta-1,3-dienyl)pyridine (**19a**): yield: 0.34 g (60%). Mp 37–39 °C.  $^1\text{H}$  NMR: 7.40 (ddd,  $^3J_{\text{HH}} = 7.6$ ,  $^3J_{\text{HH}} = 4.7$ ,  $^4J_{\text{HH}} = 1.2$ ,  $1\text{H}_{\text{arom.}}$ ); 7.49 (d,  $^3J_{\text{HH}} = 14.8$ , 1H); 7.60 (d,  $^3J_{\text{HH}} = 7.6$ ,  $1\text{H}_{\text{arom.}}$ ); 7.66 (d,  $^3J_{\text{HH}} = 12.0$ , 1H); 7.80 (dm,  $^3J_{\text{HH}} = 14.8$ , 1H); 7.87 (td,  $^3J_{\text{HH}} = 7.6$ ,  $^4J_{\text{HH}} = 1.8$ ,  $1\text{H}_{\text{arom.}}$ ); 8.67 (dm,  $^3J_{\text{HH}} = \text{ca. } 4.7$ ,  $1\text{H}_{\text{arom.}}$ ).  $^{19}\text{F}$  NMR:  $-53.3$  (qdd,  $^4J_{\text{FF}} = 6.9$ ;  $^4J_{\text{HF}} = 2.2$ ,  $^5J_{\text{HF}} = 1.0$ , 3F);  $-59.1$  (qd,  $^4J_{\text{FF}} = 6.9$ ;  $^5J_{\text{HF}} = 1.0$ , 3F). MS:  $m/z$  (rel. int., ion): 267 (39,  $M^+$ ); 248 [17, ( $M - \text{F}$ ) $^+$ ]; 228 [2, ( $\text{C}_{11}\text{H}_6\text{F}_4\text{N}$ ) $^+$ ]; 198 [100, ( $M - \text{CF}_3$ ) $^+$ ]; 178 [17, ( $\text{C}_{10}\text{H}_6\text{F}_2\text{N}$ ) $^+$ ]; 148 (5); 128 (5); 104 (3). Analysis: found: C, 49.5; H, 2.5; F, 42.4%. Calculated for  $\text{C}_{11}\text{H}_7\text{F}_6\text{N}$  (267.17): C, 49.4; H, 2.6; F, 42.7%.

3-(5,5,5-Trifluoro-4-trifluoromethylpenta-1,3-dienyl)pyridine (**19b**): yield: 1.24 g (54%). Mp 54–55 °C.  $^1\text{H}$  NMR: ( $\text{C}_2\text{D}_6\text{CO}$ ): 7.40 (ddd,  $^3J_{\text{HH}} = 7.6$ ,  $^3J_{\text{HH}} = 4.7$ ,  $^4J_{\text{HH}} = 1.2$ ,  $1\text{H}_{\text{arom.}}$ ); 7.49 (d,  $^3J_{\text{HH}} = 14.8$ , 1H); 7.60 (d,  $^3J_{\text{HH}} = 7.6$ ,  $1\text{H}_{\text{arom.}}$ ); 7.66 (d,  $^3J_{\text{HH}} = 12.0$ , 1H); 7.80 (dm,  $^3J_{\text{HH}} = 14.8$ , 1H); 7.87 (td,  $^3J_{\text{HH}} = 7.6$ ,  $^4J_{\text{HH}} = 1.8$ ,  $1\text{H}_{\text{arom.}}$ ); 8.67 (dm,  $^3J_{\text{HH}} = \text{ca. } 4.7$ ,  $1\text{H}_{\text{arom.}}$ ).  $^{19}\text{F}$  NMR:  $-53.3$  (qdd,  $^4J_{\text{FF}} = 6.9$ ;  $^4J_{\text{HF}} = 2.2$ ,  $^5J_{\text{HF}} = 1.0$ , 3F);  $-59.1$  (qd,  $^4J_{\text{FF}} = 6.9$ ;  $^5J_{\text{HF}} = 1.0$ , 3F). MS:  $m/z$  (rel. int., ion): 267 (39,  $M^+$ ); 248 [17, ( $M - \text{F}$ ) $^+$ ]; 228 [2, ( $\text{C}_{11}\text{H}_6\text{F}_4\text{N}$ ) $^+$ ]; 198 [100, ( $M - \text{CF}_3$ ) $^+$ ]; 178 [17, ( $\text{C}_{10}\text{H}_6\text{F}_2\text{N}$ ) $^+$ ]; 148 (5); 128 (5); 104 (3). Analysis: found: C, 49.5; H, 2.5; F, 42.4%. Calculated for  $\text{C}_{11}\text{H}_7\text{F}_6\text{N}$  (267.17): C, 49.4; H, 2.6; F, 42.7%.

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