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Reaction of $CBrF_2$–$CBrF_2$ with hydrazones of aromatic aldehydes Novel efficient synthesis of fluorocontaining alkanes, alkenes and alkynes

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Abstract

An olefination of hydrazones of aromatic aldehydes by $CBrF_2$–$CBrF_2$ under copper catalysis was investigated. In situ prepared aldehydes hydrazones were converted to (3-bromo-2,2,3,3-tetrafluoropropyl)arenes by reaction with $CBrF_2$–$CBrF_2$ in the presence of CuCl. Subsequent elimination of HF by sodium hydroxide resulted in stereospecific formation of fluorocontaining alkenes. Elimination proceeds stereoselectively, only *Z*-isomers of alkenes are formed. Elimination of two molecules of HF from (3-bromo-2,2,3,3-tetrafluoropropyl)arenes by treatment with potassium *tert*-butoxide leads to formation of (bromodifluoromethyl)alkynes. As a result a simple and efficient transformation of aromatic aldehydes to range of various fluorinated alkanes, alkenes and alkynes was elaborated.

Keywords: Perfluoroalkanes; Dibromotetrafluoroethane; Catalysis; Copper; Carbonyl compounds; Olefination

1. Introduction

Fluorine-containing drugs and pesticides have achieved an increasing interest in modern bioorganic chemistry due to their remarkable biological activity [1,2]. Extensive studies have been made to develop a cheap and efficient synthetic methodology for the synthesis of various organofluorine compounds. Utilization of new reagents and improved techniques for the selective introduction of fluorine or fluorinated synthons has become a major target in organofluorine chemistry.

2. Results and discussion

Recently, we reported a novel catalytic olefination reaction (COR) of aldehydes and ketones [3–10]. It was found that *N*-unsubstituted hydrazones of carbonyl compounds could be smoothly transformed into the various substituted alkenes by treatment with polyhalogenalkanes in the presence of catalytic amounts of CuCl. At the presented paper we investigated the olefination of aromatic aldehydes (**1**) with $CBrF_2$–$CBrF_2$, widely used as halogenated fire agent.

Previously $CBrF_2$–$CBrF_2$ was chemically used as C_2-fluorocontaining block in radical addition reactions to alkenes and alkynes [11–15]. Some examples of application of $CBrF_2$–$CBrF_2$ in the nucleophilic substitution have been described [16–19]. Also this halon was used as bromination agent for organolithium compounds [20,21].

We found that in situ-generated hydrazones of aromatic aldehydes (**2**) are transformed to (3-bromo-2,2,3,3-tetrafluoropropyl)arenes (**3**) by reaction with $CBrF_2CBrF_2$ and CuCl as a catalyst (Scheme 1). This reaction is the first example of formation of products without double C–C bond by the catalytic olefination reaction.

We investigated the reaction of $CBrF_2$–$CBrF_2$ with range of aromatic aldehydes in the same conditions (ethanol-ethylenediamine) and found that the corresponding (3-bromo-2,2,3,3-tetrafluoropropyl)arenes (**3a–h**) were obtained in 20–48% yield (Table 1). Both aldehydes bearing electron-donating and electron-withdrawing groups can be

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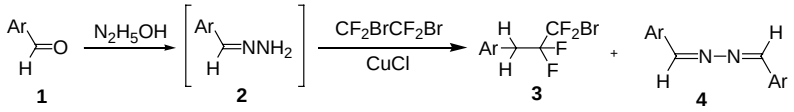
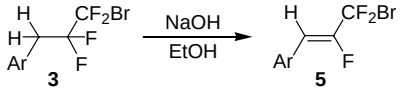


Scheme 1.



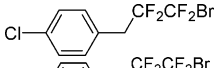
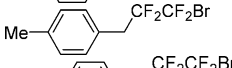
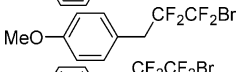
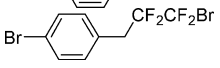
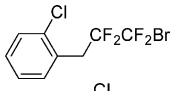
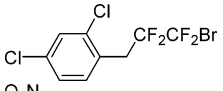
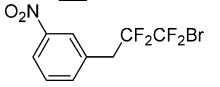
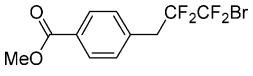
Scheme 2.

converted to the corresponding (3-bromo-2,2,3,3-tetrafluoropropyl)arenes (**3a**–**h**) by proposed method. In spite of moderate yields of target products the procedure is extremely simple and straightforward. Recently we found that only corresponding *sym*-azines of carbonyl compounds were side products of COR. In some cases corresponding *sym*-azines (**4a**–**c**) were isolated from the reaction mixture. It was found that total yield of **3** and **4** usually is close to quantitative (Table 1).

Base-promoted elimination of HF from (3-bromo-2,2,3,3-tetrafluoropropyl)arenes (**3**) permits to elaborate also synthesis of new types of alkenes and alkynes. We found that treatment of the range of alkanes (**3**) with NaOH in ethanol leads to elimination of HF and formation of corresponding fluorocontaining alkenes (**5**) in high to quantitative yield (Scheme 2). Formation of alkenes (**5**) proceeds with excellent stereoselectivity, only a *Z*-isomers of alkenes are obtained in all cases (Table 2). High diastereoselectivity can be explained by space hindrance for *syn*-configuration of bulky CF_2Br and Ph groups in transition state. It should be noted that in the case of 4-carbmethoxy substituted alkane (**3h**) both *trans*-esterification and elimination of HF proceeds simultaneously to form the corresponding 4-carbethoxy substituted alkene (**5h**).

Treatment of (3-bromo-2,2,3,3-tetrafluoropropyl)arenes (**3**) with more strong base such as *t*-BuOK leads to elimination of two molecules of HF (Scheme 3). Corresponding alkynes (**6**) bearing CF_2Br fragment were obtained as a result (Table 3). Previously similar alkynes was synthesized

Table 1
Synthesis of (3-bromo-2,2,3,3-tetrafluoropropyl)arenes from aromatic aldehydes

Entry	Product **3**	Isolated yield (%)		
		3	**4**	Total
3a		43	51	94
3b		30	63	93
3c		20	69	89
3d		40	[a]	[a]
3e		31	[a]	[a]
3f		39	[a]	[a]
3g		43	[a]	[a]
3h		48	[a]	[a]

[a] The yield of corresponding azines was not determined.

Table 2
Synthesis of (3-bromo-2,2,3-trifluoroprop-1-en-1-yl)arenes (**5**)

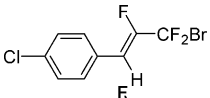
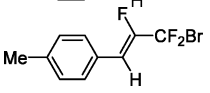
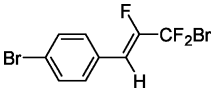
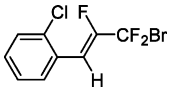
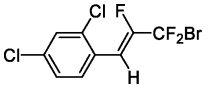
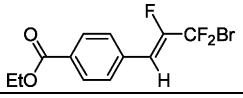
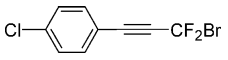
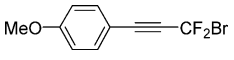
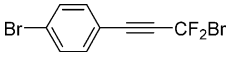
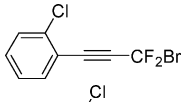
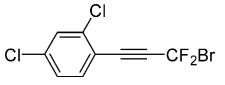
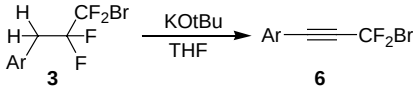
Entry	Alkene	Isolated yield (%)
5a		97
5b		95
5d		92
5e		85
5f		88
5h		83

Table 3
Synthesis of (3-bromo-3,3-difluoroprop-1-yn-1-yl)arenes (**6**)

Entry	Alkene	Isolated yield (%)
6a		80
6c		74
6d		77
6e		85
6f		79



Scheme 3.

by Wakselman and coworkers [22] and Fried and coworkers [23] via the reaction of lithiated alkynes with dibromodifluoromethane. The alkynes have been used in the synthesis of analogues of biomolecules and interesting starting materials. Mild conditions, simplicity of the reaction procedure and high yields of products are significant features of reaction proposed.

All these classes of fluorinated alkanes and alkenes were unknown previously. Alkenes (**5**) and alkynes (**6**) contains very active (mobile) bromine in allyl or propargyl position. We believe that both alkenes and alkynes can be important precursors for the preparation of functionalized organofluorine compounds via bromine substitution. Reported method of halons transformation to valuable products of organic synthesis can be applied as green chemistry process, because utilization of halogenated hydrocarbons is an actual ecological problem.

3. Conclusion

In summary we elaborated novel efficient one-pot method for the preparation of unknown class of fluoro-containing compounds—(3-bromo-2,2,3,3-tetrafluoropropyl)arenes (**3**)—from aromatic aldehydes. Mild conditions and simplicity of the reaction procedure are significant features of the presented method. We investigated synthetic scope of (3-bromo-2,2,3,3-tetrafluoropropyl)arenes and elaborated novel method for synthesis of new fluorinated alkenes (**5**) and alkynes (**6**). Moreover, new unusual route of the catalytic olefination reaction that leads to saturated products was found.

4. Experimental

NMR spectra were recorded on a Varian VXR-400 spectrometer in $CDCl_3$ with TMS and CCl_3F as an internal standard. The IR spectra were obtained with UR-20 spectrometer. Mass spectra were recorded on a Finnigan SSQ7000 mass spectrometer. Known azines (**4a–c**) were characterized by comparison of their spectral and physical data with literature [3–10]. Column chromatography was performed on silica gel (63–200 mesh, Merck).

*4.1. General procedure for synthesis of (3-bromo-2,2,3,3-tetrafluoropropyl)arenes (**3a–h**)*

A solution of aromatic aldehyde (50 mmol) in EtOH (100 mL) was added with stirring dropwise to a solution of hydrazine hydrate (2.5 mL, 50 mmol) in EtOH (50 mL) and the mixture was stirred until aldehyde disappeared (3 h, TLC monitoring). Then freshly purified CuCl [24] (500 mg, 5 mmol) and 1,2-ethylenediamine (17 mL, 250 mmol) were added. After 10 min $CBrF_2$–$CBrF_2$ (27 mL, 250 mmol) was added dropwise. After addition of $CBrF_2$–$CBrF_2$ the reaction mixture was stirred for 5 h at 50 °C, then cooled and quenched with hydrochloric acid (5%) (500 mL). Reaction products were extracted with CH_2Cl_2 (100 mL × 5). Extracts were dried over sodium sulphate, CH_2Cl_2 was evaporated and the residue was purified by column chromatography.

*4.1.1. 1-(3-Bromo-2,2,3,3-tetrafluoropropyl)-4-chlorobenzene (**3a**)*

Colorless oil; R_f (hexane) 0.4; IR (KBr): ν 1500, 1600, 2950; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.26 (2H, t, $J = 18.2$ Hz, CH_2), 7.15 (2H, d, $J = 7.9$ Hz, Ar), 7.24 (2H, d, $J = 7.9$ Hz, Ar); ^{13}C NMR (100 MHz, $CDCl_3$): δ 36.07 (t, $J_{CF} = 22.9$ Hz, CH_2), 115.66 (tt, $J_{CF} = 254.8$ Hz, $J_{CF} = 31.3$ Hz, CF_2), 117.54 (tt, $J_{CF} = 311.3$ Hz, $J_{CF} = 39.7$ Hz, CF_2Br), 127.95, 128.78, 132.00, 134.26; ^{19}F NMR (376.27 MHz, $CDCl_3$/CCl_3F): δ −65.61 (s, CF_2Br), −111.13 (t, $J_{HF} = 18.2$ Hz, CF_2). EIMS (probe), 70 eV, *m/z* (rel. int.): 304 $[M]^+$ (4), 225 $[M-Br]^+$ (1), 205 $[M-Br-H-F]^+$ (2), 185 $[M-Br-2H-2F]^+$ (2), 169 $[M-Cl-C_2F_4]^+$ (2), 125 $[M-Br-C_2F_4]^+$ 100. Anal. Calcd. for $C_9H_6BrClF_4$: C, 35.38; H, 1.98. Found: C, 35.6; H, 1.9.

*4.1.2. 1-(3-Bromo-2,2,3,3-tetrafluoropropyl)-4-methylbenzene (**3b**)*

Colorless oil; R_f (hexane) 0.45; IR (KBr): ν 1500, 1600, 2950. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.37 (3H, s, Me), 3.35 (2H, t, $J = 18.2$ Hz, CH_2), 7.19 (4H, s, Ar); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.08 (Me), 36.25 (t, $J_{CF} = 22.9$ Hz, CH_2), 115.77 (tt, $J_{CF} = 254.8$ Hz, $J_{CF} = 31.3$ Hz, CF_2), 117.84 (tt, $J_{CF} = 311.3$ Hz, $J_{CF} = 39.7$ Hz, CF_2Br), 126.40, 129.27, 130.59, 137.83; ^{19}F NMR (376.27 MHz, $CDCl_3$/CCl_3F): δ −65.44 (s, CF_2Br), −111.16 (t, $J_{HF} = 18.2$ Hz, CF_2). EIMS (probe), 70 eV, *m/z* (rel. int.): 284 $[M]^+$ (3), 205 $[M-Br]^+$ (1), 185 $[M-Br-H-F]^+$ (2), 165 $[M-Br-2H-2F]^+$ (2), 151 $[M-Br-2H-2F-CH_2]^+$ (1), 133 $[M^+-Br-3F-3H-C]$ (1), 105 $[M^+-Br-C_2F_4]$ (100), 91 $[C_7H_7]^+$ (3). Anal. Calcd. for $C_9H_{10}BrF_4$: C, 42.13; H, 3.18. Found: C, 42.5; H, 3.3.

*4.1.3. 1-(3-Bromo-2,2,3,3-tetrafluoropropyl)-4-methoxybenzene (**3c**)*

Colorless oil; R_f (hexane) 0.2; IR (KBr): ν 1520, 1600, 2850 (CH_3O), 2950; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.31 (2H, t, $J = 18.2$ Hz, CH_2), 3.80 (3H, s, OMe), 6.89 (2H, d, $J = 8.5$ Hz, Ar), 7.21 (2H, d, $J = 8.5$ Hz, Ar); ^{13}C NMR (100 MHz, $CDCl_3$): δ 35.84 (t, $J_{CF} = 22.9$ Hz, CH_2), 55.18 (OMe), 113.99, 115.79 (tt, $J_{CF} = 254.8$ Hz, $J_{CF} = 31.3$ Hz, CF_2), 117.83 (tt, $J_{CF} = 311.3$ Hz, $J_{CF} = 39.7$ Hz, CF_2Br),

121.38, 131.77, 159.45 (C–OMe); ^{19}F NMR (376.27 MHz, $CDCl_3/CCl_3F$): δ −65.41 (s, CF_2Br), −111.29 (t, J_{HF} = 18.2 Hz, CF_2). EIMS (probe), 70 eV, *m/z* (rel. int.): 300 $[M]^+$ (2), 221 $[M-Br]^+$ (1), 201 $[M-Br-H-F]^+$ (1), 181 $[M-Br-2H-2F]^+$ (1), 170 $[M-Br-2F-C-H]^+$ (1), 121 $[M-Br-C_2F_4]^+$ (100), 91 $[C_7H_7]^+$ (4). Anal. Calcd. for $C_9H_{10}BrF_4O$: C, 39.89; H, 3.01. Found: C, 39.6; H, 3.0.

*4.1.4. 1-Bromo-4-(3-bromo-2,2,3,3-tetrafluoropropyl)benzene (**3d**)*

Colorless oil; R_f (hexane) 0.45; IR (KBr): *v* 1510, 1600, 2950. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.33 (2H, t, J = 18.2 Hz, CH_2), 7.16 (2H, d, J = 7.9 Hz, Ar), 7.49 (2H, d, J = 7.9 Hz, Ar); ^{13}C NMR (100 MHz, $CDCl_3$): δ 36.20 (t, J_{CF} = 22.9 Hz, CH_2), 115.66 (tt, J_{CF} = 254.8 Hz, J_{CF} = 31.3 Hz, CF_2), 117.52 (tt, J_{CF} = 311.3 Hz, J_{CF} = 39.7 Hz, CF_2Br), 128.48, 130.79, 131.76, 132.32; ^{19}F NMR (376.27 MHz, $CDCl_3/CCl_3F$): δ −65.62 (s, CF_2Br), −111.10 (t, J_{HF} = 18.2 Hz, CF_2). EIMS (probe), 70 eV, *m/z* (rel. int.): 348 $[M]^+$ (4), 269 $[M-Br]^+$ (1), 249 $[M-Br-H-F]^+$ (2), 218 $[M-CF_2Br-H]^+$ (1), 169 $[M-Br-C_2F_4]^+$ (100), 140 $[M-CF_2Br-Br]^+$ (10). Anal. Calcd. for $C_9H_6Br_2F_4$: C, 30.89; H, 1.73. Found: C, 31.1; H, 1.8.

*4.1.5. 1-(3-Bromo-2,2,3,3-tetrafluoropropyl)-2-chlorobenzene (**3e**)*

Colorless oil; R_f (hexane) 0.45; IR (KBr): *v* 1500, 1600, 2950; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.53 (2H, t, J = 18.2 Hz, CH_2), 7.15–7.23 (2H, m, Ar), 7.29 (1H, d, J = 8.5 Hz, Ar), 7.35 (1H, dd, J = 7.6 Hz, J = 1.5 Hz, Ar); ^{13}C NMR (100 MHz, $CDCl_3$): δ 33.48 (t, J_{CF} = 21.4 Hz, CH_2), 115.69 (tt, J_{CF} = 254.8 Hz, J_{CF} = 31.3 *Hz*, CF_2), 117.63 (tt, J_{CF} = 311.3 Hz, J_{CF} = 39.7 Hz, CF_2Br), 126.86, 127.95, 129.59, 129.89, 132.65, 135.63; ^{19}F NMR (376.27 MHz, $CDCl_3/CCl_3F$): δ −66.04 (s, CF_2Br), −110.79 (t, J_{HF} = 18.2 Hz, CF_2). EIMS (probe), 70 eV, *m/z* (rel. int.): 304 $[M]^+$ (1), 225 $[M-Br]^+$ (1), 205 $[M-Br-H-F]^+$ (3), 185 $[M-Br-2H-2F]^+$ (2), 169 $[M-Cl-C_2F_4]^+$ (4), 125 $[M-Br-C_2F_4]^+$ (100). Anal. Calcd. for $C_9H_6BrClF_4$: C, 35.38; H, 1.98. Found: C, 35.1; H, 2.0.

*4.1.6. 1-(3-Bromo-2,2,3,3-tetrafluoropropyl)-2,4-dichlorobenzene (**3f**)*

Colorless oil; R_f (hexane) 0.4; IR (KBr): *v* 1480, 1600, 2950; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.49 (2H, t, J = 17.9 Hz, CH_2), 7.17 (1H, dd, J = 8.2 Hz, J = 2.1 Hz, Ar), 7.22 (1H, d, J = 8.2 Hz, Ar), 7.37 (1H, d, J = 2.1 Hz, Ar); ^{13}C NMR (100 MHz, $CDCl_3$): δ 33.06 (t, J_{CF} = 22.9 Hz, CH_2), 115.81 (tt, J_{CF} = 254.8 Hz, J_{CF} = 32.0 Hz, CF_2), 117.43 (tt, J_{CF} = 311.3 Hz, J_{CF} = 39.7 Hz, CF_2Br), 126.55, 127.28, 129.75, 133.32, 135.02, 136.34; ^{19}F NMR (376.27 MHz, $CDCl_3/CCl_3F$): δ −66.15 (s, CF_2Br), −110.77 (t, J_{HF} = 17.9 Hz, CF_2). EIMS (probe), 70 eV, *m/z* (rel. int.): 338 $[M]^+$ (1), 259 (1) $[M-Br]^+$, 239 $[M-Br-H-F]^+$ (2), 219 $[M-Br-2H-2F]^+$ (1), 203 $[M-Cl-Br-HF]^+$ (1), 159 $[M-Br-C_2F_4]^+$ (100). Anal. Calcd. for $C_9H_5BrCl_2F_4$: C, 31.80; H, 1.48. Found: C, 32.0; H, 1.5.

*4.1.7. 1-(3-Bromo-2,2,3,3-tetrafluoropropyl)-3-nitrobenzene (**3g**)*

Colorless oil; R_f (hexane/CH_2Cl_2 1/1) 0.6; IR (KBr): *v* 1480, 1530 (NO_2), 1600, 2950; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.50 (2H, t, J = 17.7 Hz, CH_2), 7.55 (1H, dd, J = 8.2 Hz, J = 7.6 Hz, Ar), 7.64 (1H, d, J = 7.6 Hz, Ar), 8.18 (1H, s, Ar), 8.21 (1H, d, J = 8.2 Hz, Ar); ^{13}C NMR (100 MHz, $CDCl_3$): δ 36.34 (t, J_{CF} = 22.9 Hz, CH_2), 115.57 (tt, J_{CF} = 254.8 Hz, J_{CF} = 31.3 Hz, CF_2), 117.10 (tt, J_{CF} = 311.3 Hz, J_{CF} = 39.7 Hz, CF_2Br), 123.26, 125.60, 129.60, 131.50, 136.73, 148.31; ^{19}F NMR (376.27 MHz, $CDCl_3/CCl_3F$): δ −65.90 (s, CF_2Br), −110.99 (t, J_{HF} = 17.7 Hz, CF_2). EIMS (probe), 70 eV, *m/z* (rel. int.): 315 $[M]^+$ (30), 285 (1) $[M-HF]^+$, 269 $[M-NO_2]^+$ (15), 236 $[M-Br]^+$ (2), 205 $[M-Br-F-C-H]^+$ (8), 190 $[M-Br-NO_2]^+$ (12), 169 $[M-NO_2-C_2F_4]^+$ (38), 136 $[M-Br-C_2F_4]^+$ (100), 109 $[C_7H_6F]^+$ (63), 90 $[M-Br-C_2F_4-NO_2]^+$ (34). Anal. Calcd. for $C_9H_6BrF_4NO_2$: C, 34.60; H, 1.91. Found: C, 34.9; H, 1.9.

*4.1.8. Methyl 4-(3-bromo-2,2,3,3-tetrafluoropropyl)benzoate (**3h**)*

Colorless oil; R_f (hexane) 0.2; IR (KBr): *v* 1510, 1600, 1740 (C=O), 2950, 2980 (OCH_3); ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.33 (2H, t, J = 18.2 Hz, CH_2), 3.82 (3H, s, OCH_3), 7.27 (2H, d, J = 8.5 Hz, Ar), 7.92 (2H, d, J = 8.5 Hz, Ar); ^{13}C NMR (100 MHz, $CDCl_3$): δ 36.63 (t, J_{CF} = 22.9 Hz, CH_2), 52.10 (OCH_3), 115.76 (tt, J_{CF} = 254.8 Hz, J_{CF} = 31.3 Hz, CF_2), 117.48 (tt, J_{CF} = 311.3 Hz, J_{CF} = 39.7 Hz, CF_2Br), 129.74, 130.04, 130.74, 134.59, 166.58 (C=O); ^{19}F NMR (376.27 MHz, $CDCl_3/CCl_3F$): δ −65.64 (s, CF_2Br), −110.72 (t, J_{HF} = 18.2 Hz, CF_2). EIMS (probe), 70 eV, *m/z* (rel. int.): 328 $[M]^+$ (16), 297 $[M-OCH_3]^+$ (100), 269 $[M-CO_2Me]^+$ (4), 217 $[M-Br-H-OMe]^+$ (2), 189 $[M-Br-H-CO_2Me]^+$ (10), 169 $[M-Br-CO_2Me-2H-F]^+$ (20), 149 $[M-Br-C_2F_4]^+$ (34), 121 $[C_8H_6F]^+$ (23), 109 $[C_7H_6F]^+$ (31). Anal. Calcd. for $C_{11}H_9BrF_4O_2$: C, 40.15; H, 2.76. Found: C, 40.1; H, 2.7.

*4.2. General procedure for synthesis of (3-bromo-2,3,3-trifluoro-1-propenyl)arenes (**5**)*

A 50% NaOH (0.1 mL, 2.5 mmol) was added to a solution of alkane (**3**) (1 mmol) in EtOH (5 mL). The mixture was refluxed with stirring until alkane disappeared (2–5 h, TLC monitoring). Then the reaction mixture cooled and quenched with hydrochloric acid (5%) (50 mL) and extracted with CH_2Cl_2 (20 mL × 3). Extracts were dried over sodium sulphate, CH_2Cl_2 was evaporated and the residue was purified by column chromatography.

*4.2.1. 1-[(1Z)-3-Bromo-2,3,3-trifluoro-1-propenyl]-4-chlorobenzene (**5a**)*

Colorless oil; R_f (hexane) 0.7; IR (KBr): ν 1500, 1600, 1700 (C=C), 2950; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.25 (1H, d, $J = 34.9$ Hz, =CH–), 7.37 (2H, d, $J = 8.5$ Hz, Ar), 7.50 (2H, d, $J = 8.5$ Hz, Ar); ^{13}C NMR (100 MHz, $CDCl_3$): δ 107.57–107.63 (m, =CH–), 111.77 (td, $J_{CF} = 302.2$ Hz, $J_{CF} = 44.2$ Hz, CF_2Br), 128.38 (d, $J_{CF} = 4.6$ Hz), 129.33, 131.09 (d, $J_{CF} = 7.6$ Hz), 135.85, 149.84 (dt, $J_{CF} = 267.0$ Hz, $J_{CF} = 29.0$ Hz, =CF–); ^{19}F NMR (376.27 MHz, $CDCl_3/CCl_3F$): δ −55.48 (d, $J_{FF} = 19.8$ Hz, CF_2Br), −124.59 (dt, $J_{HF} = 34.9$ Hz, $J_{FF} = 19.8$ Hz, =CF–). EIMS (probe), 70 eV, *m/z* (rel. int.): 284 $[M]^+$ (3), 205 $[M-Br]^+$ (100), 185 $[M-Br-H-F]^+$ (80), 169 $[M-Br-Cl-H]^+$ (43), 151 $[M-Br-Cl-H-F]^+$ (20). Anal. Calcd. for $C_9H_5BrClF_3$: C, 37.86; H, 1.77. Found: C, 37.9; H, 1.7.

*4.2.2. 1-[(1Z)-3-Bromo-2,3,3-trifluoro-1-propenyl]-4-methylbenzene (**5b**)*

Colorless oil; R_f (hexane) 0.75; IR (KBr): ν 1500, 1600, 1700 (C=C), 2950; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.41 (3H, s, Me), 6.29 (1H, d, $J = 35.5$ Hz, =CH–), 7.24 (2H, d, $J = 8.2$ Hz, Ar), 7.50 (2H, d, $J = 8.2$ Hz, Ar); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.42 (Me), 108.67–108.73 (m, =CH–), 112.15 (td, $J_{CF} = 302.2$ Hz, $J_{CF} = 44.1$ Hz, CF_2Br), 127.04 (d, $J_{CF} = 4.6$ Hz), 129.62, 129.78 (d, $J_{CF} = 7.6$ Hz), 139.78, 148.76 (dt, $J_{CF} = 264.0$ Hz, $J_{CF} = 29.0$ Hz, =CF–); ^{19}F NMR (376.27 MHz, $CDCl_3/CCl_3F$): δ −54.85 (d, $J_{FF} = 19.8$ Hz, CF_2Br), −126.44 (dt, $J_{HF} = 35.5$ Hz, $J_{FF} = 19.8$ Hz, =CF–). EIMS (probe), 70 eV, *m/z* (rel. int.): 264 $[M]^+$ (3), 185 $[M-Br]^+$ (100), 165 $[M-Br-H-F]^+$ (80), 151 $[M-Br-3H-F-C]^+$ (10), 145 $[M-Br-2H-2F]^+$ (10), 133 $[M-Br-2H-2F-C]^+$ (16), 115 $[M^+-Br-H-3F-C]$ (14). Anal. Calcd. for $C_{10}H_8BrF_3$: C, 45.31; H, 3.04. Found: C, 45.0; H, 3.1.

*4.2.3. 1-Bromo-4-[(1Z)-3-bromo-2,3,3-trifluoro-1-propenyl] benzene (**5d**)*

Colourless oil; R_f (Hexane) 0.7. IR (KBr); 1500, 1600, 1700 (C=C), 2950. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.24 (1H, d, $J = 34.6$ Hz, =CF–), 7.42 (2H, d, $J = 8.8$ Hz, Ar), 7.53 (2H, d, $J = 8.8$ Hz, Ar). ^{13}C NMR (100 MHz, $CDCl_3$): δ 107.68–107.73 (m, =CH–), 111.69 (td, $J_{CF} = 302.1$ Hz, $J_{CF} = 44.7$ Hz, CF_2Br), 123.85, 128.72 (d, $J_{CF} = 4.6$ Hz), 131.16 (d, $J_{CF} = 7.6$ Hz), 132.15, 149.60 (dt, $J_{CF} = 265.5$ Hz, $J_{CF} = 29.0$ Hz, =CF–). ^{19}F NMR (376.27 MHz, $CDCl_3/CCl_3F$): δ —55.52 (d, $J_{FF} = 19.8$ Hz, CF_2Br), −124.69 (dt, $J_{HF} = 34.6$ Hz, $J_{FF} = 19.8$ Hz, =CF–). EIMS (probe), 70 eV, *m/z* (rel. int.): 328 $[M]^+$ (1), 249 $[M-Br]^+$ (24), 229 $[M-Br-H-F]^+$ (2), 170 $[M-2Br]^+$ (100), 151 $[M-2Br-F-H]^+$ (32), 120 $[M-2Br-2F-H-C]^+$ (8). Anal. Calcd. for $C_9H_5Br_2F_3$: C, 32.76; H, 1.53. Found: C, 32.5; H, 1.5.

*4.2.4. 1-[(1Z)-3-Bromo-2,3,3-trifluoro-1-propenyl]-2-chlorobenzene (**5e**)*

Colorless oil; R_f (hexane) 0.7; IR (KBr): ν 1490, 1600, 1700 (C=C), 2950. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.78 (1H, d, $J = 34.6$ Hz, =CF–), 7.28–7.33 (2H, m, Ar), 7.41–7.45 (1H, m, Ar), 7.81–7.83, (1H, m, Ar); ^{13}C NMR (100 MHz, $CDCl_3$): δ 104.60–104.75 (m, =CH–), 111.66 (td, $J_{CF} = 302.2$ Hz, $J_{CF} = 42.7$ Hz, CF_2Br), 127.10, 127.92 (d, $J_{CF} = 4.6$ Hz), 129.86, 130.51, 130.69 (d, $J_{CF} = 7.6$ Hz), 134.27, 149.95 (dt, $J_{CF} = 268.6$ Hz, $J_{CF} = 29.0$ Hz, =CF–); ^{19}F NMR (376.27 MHz, $CDCl_3/CCl_3F$): δ −54.45 (d, $J_{FF} = 19.8$ Hz, CF_2Br), −124.86 (dt, $J_{HF} = 34.6$ Hz, $J_{FF} = 19.8$ Hz, =CF–). EIMS (probe), 70 eV, *m/z* (rel. int.): 284 $[M]^+$ (8), 205 $[M-Br]^+$ (100), 185 $[M-Br-H-F]^+$ (67), 169 $[M-Br-H-Cl]^+$ (35), 151 $[M-Br-Cl-F-H]^+$ (16), 120 $[M-Br-2F-Cl-H-C]^+$ (8). Anal. Calcd. for $C_9H_5BrClF_3$: C, 37.86; H, 1.77. Found: C, 37.7; H, 1.8.

*4.2.5. 1-[(1Z)-3-Bromo-2,3,3-trifluoro-1-propenyl]-2,4-dichlorobenzene (**5f**)*

Colorless oil; R_f (hexane) 0.7; IR (KBr): ν 1480, 1600, 1700 (C=C), 2950; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.70 (1H, d, $J = 34.0$ Hz, =CF–), 7.29 (1H, dd, $J = 8.5$ Hz, $J = 2.1$ Hz, Ar), 7.44 (1H, d, $J = 2.1$ Hz, Ar), 7.75 (1H, d, $J = 8.5$ Hz, Ar); ^{13}C NMR (100 MHz, $CDCl_3$): δ 103.73–103.78 (m, =CH–), 111.45 (td, $J_{CF} = 302.1$ Hz, $J_{CF} = 42.7$ Hz, CF_2Br), 126.46 (d, $J_{CF} = 4.6$ Hz), 127.57, 129.77, 131.30 (d, $J_{CF} = 7.6$ Hz), 134.91, 135.87, 150.44 (dt, $J_{CF} = 268.6$ Hz, $J_{CF} = 29.0$ Hz, =CF–); ^{19}F NMR (376.27 MHz, $CDCl_3/CCl_3F$): δ −55.71 (d, $J_{FF} = 16.5$ Hz, CF_2Br), −123.75 (dt, $J_{HF} = 34.0$ Hz, $J_{FF} = 16.5$ Hz, =CF–). EIMS (probe), 70 eV, *m/z* (rel. int.): 318 $[M]^+$ (3), 239 $[M-Br]^+$ (100), 219 $[M-Br-H-F]^+$ (40), 204 $[M-Cl-Br]^+$ (37), 185 $[M-Cl-Br-F]^+$ (12), 169 $[M-Br-2Cl]^+$ (72), 154 $[M-Br-Cl-C-2F]^+$ (12), 149 $[M-Br-2Cl-F-H]^+$ (8), 119 $[C_8H_4F]^+$ (14). Anal. Calcd. for $C_9H_5BrClF_3$: C, 33.79; H, 1.26. Found: C, 33.6; H, 1.3.

*4.2.6. Ethyl 4-[(1Z)-3-bromo-2,3,3-trifluoro-1-propenyl]benzoate (**5h**)*

Colorless oil; R_f (hexane) 0.15; IR (KBr): ν 1520, 1600, 1700 (C=C), 1740 (C=O), 2950, 2990 (OEt); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.39 (3H, t, $J = 7.0$ Hz, CH_3), 4.37 (2H, q, $J = 7.0$ Hz, –CH_2O–), 6.32 (1H, d, $J = 34.6$ Hz, =CF–), 7.60 (2H, d, $J = 8.2$ Hz, Ar), 8.05 (2H, d, $J = 8.2$ Hz, Ar); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.22 (CH_3), 61.18 (–CH_2O–), 107.70–107.95 (m, =CF–), 111.52 (td, $J_{CF} = 302.1$ Hz, $J_{CF} = 44.3$ Hz, CF_2Br), 129.55 (d, $J_{CF} = 7.6$ Hz), 126.67 (d, $J_{CF} = 4.6$ Hz), 129.92, 133.93, 150.24 (dt, $J_{CF} = 268.6$ Hz, $J_{CF} = 29.0$ Hz, =CF–), 165.76 (C=O). ^{19}F NMR (376.27 MHz, $CDCl_3/CCl_3F$): δ −55.54 (d, $J_{FF} = 16.5$ Hz, CF_2Br), −122.69 (dt, $J_{HF} = 34.6$ Hz, $J_{FF} = 16.5$ Hz, =CF–). EIMS (probe), 70 eV, *m/z* (rel. int.): 322 $[M]^+$ (1), 277

$[M-CO_2Et]^+$ (2), 243 $[M-Br]^+$ (13), 215 $[M-Br-2C-5H]^+$ (3), 198 $[M-Br-OEt]^+$ (13), 169 $[M-Br-OEt-C-HF]^+$ (38), 151 $[M-Br-CO_2Et-HF]^+$ (100), 119 $[C_8H_5F]^+$ (9). Anal. Calcd. for $C_{12}H_{10}BrF_3O_2$: C, 44.61; H, 3.12. Found: C, 44.4; H, 3.1.

4.3. General procedure for synthesis of (3-bromo-3,3-difluoro-1-propynyl)arenes (**6**)

A solution of 1 M *t*-BuOK in THF (3 mL) was added dropwise to a solution of alkane (**3**) (1 mmol) in THF (2 mL) at 0 °C (water bath). The mixture was stirring until alkane disappeared (3–6 h, TLC monitoring). Then the reaction mixture quenched with hydrochloric acid (5%) (50 mL) and extracted with CH_2Cl_2 (20 mL × 3). Extracts were dried over sodium sulphate, CH_2Cl_2 was evaporated and the residue was purified by column chromatography.

4.3.1. 1-(3-Bromo-3,3-difluoro-1-propynyl)-4-chlorobenzene (**6a**)

Colorless oil; R_f (hexane) 0.75; IR (KBr): *v* 1500, 1600, 2270 (C=C), 2950; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (2H, d, $J = 8.5$ Hz, Ar), 7.50 (2H, d, $J = 8.5$ Hz, Ar); ^{13}C NMR (100 MHz, $CDCl_3$): δ 82.19 (t, $J_{CF} = 38.9$ Hz, Ar–C≡C–CF_2Br), 88.37 (t, $J_{CF} = 6.1$ Hz, Ar–C≡C–CF_2Br), 101.94 (t, $J_{CF} = 289.9$ Hz, CF_2Br), 117.55, 129.28, 133.55, 137.53; ^{19}F NMR (376.27 MHz, $CDCl_3/CCl_3F$): δ −32.64 (s, CF_2Br). EIMS (probe), 70 eV, *m/z* (rel. int.): 264 $[M]^+$ (2), 245 $[M-F]^+$ (1), 185 $[M-Br]^+$ (100), 166 $[M-Br-F]^+$ (1), 150 $[M-Br-Cl]^+$ (14), 131 $[M-Br-Cl-F]^+$ (5), 99 $[M-CF_2Br-Cl]^+$ (11). Anal. Calcd. for $C_9H_4BrClF_2$: C, 40.72; H, 1.52. Found: C, 40.6; H, 1.5.

4.3.2. 1-(3-Bromo-3,3-difluoro-1-propynyl)-4-methoxybenzene (**6c**)

Colorless oil; R_f (hexane) 0.15; IR (KBr): *v* 1520, 1600, 2230 (C≡C), 2850 (OCH_3), 2950; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.83 (3H, s, CH_3O), 6.89 (2H, d, $J = 8.8$ Hz, Ar), 7.47 (2H, d, $J = 8.8$ Hz, Ar); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.35 (MeO), 80.26 (t, $J_{CF} = 38.2$ Hz, Ar–C≡C–CF_2Br), 90.59 (t, $J_{CF} = 6.1$ Hz, Ar–C≡C–CF_2Br), 102.2 (t, $J_{CF} = 289.9$ Hz, CF_2Br), 110.64, 114.32, 133.97, 161.55 (**C**–OMe); ^{19}F NMR (376.27 MHz, $CDCl_3/CCl_3F$): δ −30.86 (s, CF_2Br). EIMS (probe), 70 eV, *m/z* (rel. int.): 260 $[M]^+$ (3), 241 $[M-F]^+$ (1), 181 $[M-Br]^+$ (100), 166 $[M-Br-Me]^+$ (13), 150 $[M-Br-OMe]^+$ (2), 138 $[M-Br-OMe-C]^+$ (22). Anal. Calcd. for $C_{10}H_7BrF_2O$: C, 46.01; H, 2.70. Found: C, 45.9; H, 2.8.

4.3.3. 1-Bromo-4-(3-bromo-3,3-difluoro-1-propynyl)benzene (**6d**)

Colorless oil; R_f (hexane) 0.75; IR (KBr): 1500, 1600, 2270 (C≡C), 2950; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (2H, d, $J = 8.5$ Hz, Ar), 7.54 (2H, d, $J = 8.5$ Hz, Ar); ^{13}C NMR (100 MHz, $CDCl_3$): δ 81.84 (t, $J_{CF} = 38.9$ Hz, Ar–C≡C–CF_2Br), 87.76 (t, $J_{CF} = 6.1$ Hz, Ar–C≡C–CF_2Br), 101.90 (t, $J_{CF} = 289.9$ Hz, CF_2Br), 117.72, 125.67, 132.07, 135.55; ^{19}F NMR (376.27 MHz, $CDCl_3/CCl_3F$): δ −32.46 (s, CF_2Br). EIMS (probe), 70 eV, *m/z* (rel. int.): 308 $[M]^+$ (2), 289 $[M-F]^+$ (1), 229 $[M-Br]^+$ (100), 150 $[M-2Br-Me]^+$ (45), 131 $[M-2Br-F]^+$ (2), 99 $[M-CF_2Br-Br]^+$ (16). Anal. Calcd. for $C_9H_4Br_2F_2$: C, 34.88; H, 1.30. Found: C, 34.7; H, 1.2.

4.3.4. 1-(3-Bromo-3,3-difluoro-1-propynyl)-2-chlorobenzene (**6e**)

Colorless oil; R_f (hexane) 0.75; IR (KBr): *v* 1490, 1600, 2270 (C–C), 2950; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 (1H, ddd, $J = 7.9$ Hz, $J = 7.6$ Hz, $J = 1.5$ Hz, Ar), 7.38 (1H, ddd, $J = 7.9$ Hz, $J = 7.6$ Hz, $J = 1.5$ Hz, Ar), 7.44 (1H, dd, $J = 7.9$ Hz, $J = 1.5$ Hz, Ar), 7.55 (1H, dd, $J = 7.9$ Hz, $J = 1.5$ Hz, Ar); ^{13}C NMR (100 MHz, $CDCl_3$): δ 82.15 (t, $J_{CF} = 38.8$ Hz, Ar–C≡C–CF_2Br), 86.50 (t, $J_{CF} = 6.1$ Hz, Ar–C≡C–CF_2Br), 101.90 (t, $J_{CF} = 289.9$ Hz, CF_2Br), 119.15, 126.69, 129.71, 131.86, 133.93, 137.11; ^{19}F NMR (376.27 MHz, $CDCl_3/CCl_3F$): δ −33.83 (s, CF_2Br). EIMS (probe), 70 eV, *m/z* (rel. int.): 264 $[M]^+$ (3), 245 $[M-F]^+$ (1), 185 $[M-Br]^+$ (100), 166 $[M-Br-F]^+$ (6), 150 $[M^+-Br-Cl]^+$ (23), 131 $[M-Br-Cl-F]^+$ (2), 99 $[M-CF_2Br-Cl]^+$ (13). Anal. Calcd. for $C_9H_4BrClF_2$: C, 40.72; H, 1.52. Found: C, 40.5; H, 1.6.

4.3.5. 1-(3-Bromo-3,3-difluoro-1-propynyl)-2,4-dichlorobenzene (**6f**)

Colorless oil; R_f (hexane) 0.7; IR (KBr): *v* 1480, 1600, 2270 (C≡C), 2950; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27 (1H, dd, $J = 8.5$ Hz, $J = 1.8$ Hz, Ar), 7.46 (1H, d, $J = 1.8$ Hz, Ar), 7.48 (1H, d, $J = 8.5$ Hz, Ar); ^{13}C NMR (100 MHz, $CDCl_3$): δ 85.33 (t, $J_{CF} = 6.1$ Hz, Ar–C≡C–CF_2Br), 85.83 (t, $J_{CF} = 38.9$ Hz, Ar–C≡C–CF_2Br), 101.75 (t, $J_{CF} = 289.9$ Hz, CF_2Br), 117.72, 127.34, 129.84, 134.46, 137.72, 137.95; ^{19}F NMR (376.27 MHz, $CDCl_3/CCl_3F$): δ −35.73 (s, CF_2Br). EIMS (probe), 70 eV, *m/z* (rel. int.): 298 $[M]^+$ (1), 281 $[M-F]^+$ (2), 219 $[M-Br]^+$ (100), 184 $[M^+-Br-Cl]^+$ (14), 165 $[M-Br-Cl-F]^+$ (4), 149 $[M-Br-2Cl]^+$ (29), 99 $[C_8H_3]^+$ (3). Anal. Calcd. for $C_9H_3BrCl_2F_2$: C, 36.04; H, 1.01. Found: C, 35.8; H, 1.1.

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