Bromofluorocarbene addition to 6-phenylbicyclo[3.2.0]hept-6-ene: characterization and formation mechanism of the products

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Abstract

Bromofluorocarbene addition to 6-phenylbicyclo[3.2.0]hept-6-ene provided fluoro-indanes such as 4,6-difluoro-5-phenylindane, 5,6-difluoro-4-phenylindane, 5,7-difluoro-4-phenylindane, 4-bromo-6-fluoro-5-phenylindane and 5-bromo-6-fluoro-4-phenylindane. The characterization the formation mechanism of the products are discussed.

Keywords: Bromofluorocarbene, carbene addition, fluoro-indanes

Introduction

Carbenes are versatile intermediates that undergo insertion, rearrangement and facile addition reactions in which their importance to synthetic chemists can hardly be overestimated.[1] The most common and thoroughly investigated reaction of carbenes is their addition to carbon-carbon double bonds, which provide ready access to cyclopropane derivatives and/or the corresponding rearranged products. Our contribution to this field is exemplified with the synthesis of bromofluoro cyclopropanes **1**, **2** and **3**, which were successfully converted to corresponding strained cyclic allenes and in turn stimulated us to attain further insights into this class of compounds.[2-4] It is also worth noting that only a few carbene reactions with small-ring alkenes have been reported.[5,6] Albeit numerous studies with open chain and cyclic alkenes larger than four-membered rings do in fact exist. Therefore, we have turned our attention to an unsymmetrical cyclobutene appendage **4** in connection with our work directed toward the synthesis of strained small-ring allenes.[7] Herein, we would like to report the results of the bromofluoro carbene addition to 6-phenylbicyclo[3.2.0]hept-6-ene **(4)**.[8]

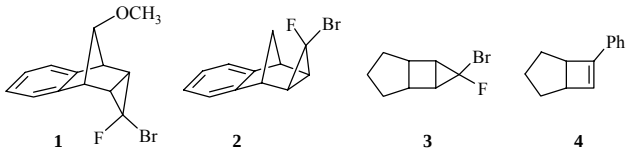
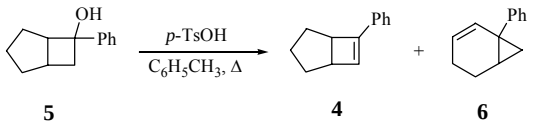


Figure 1

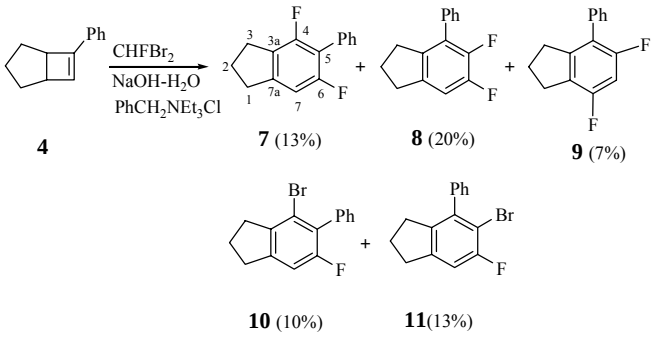
Results and Discussion

The starting material **4** was synthesized using a different route. Our research commenced with a three-step preparation of the known alcohol **5**, which was obtained by the addition of dichloroketene to cyclopentene[9] followed by dehalogenation and a reaction with phenyl magnesium bromide.[10] The acid catalyzed dehydration of alcohol **5** with *p*-toluensulphonic acid resulted in the formation of cyclobutene **4** along with norcarene **6** in a ratio of 3:1 (Scheme 1). The norcarene derivative **6** was previously synthesized in quantitative yield by the reaction of a trace amount of $BF_3(Et_2O)$ with of 1-phenyltricyclo[4.1.0.$0^{2,7}$]heptane.[8a]



Scheme 1

The presence of a cyclopropane ring in **6** was proven spectroscopically based on the coupling constants between the proton and carbon nuclei (J_{CH}) of which its size strongly depends on the s fraction of the hybridization on the carbon. From the proton coupled ^{13}C-NMR spectrum of the compound **6**, the coupling constants between the cyclopropane carbons and protons ($^1J_{CH}$) were found to be 158.4 and 160.4 Hz, which are characteristic of the cyclopropane carbons.[11]
After obtaining the desired precursor **4**, it was treated with bromofluorocarbene under phase transfer conditions. The addition of bromofluorocarbene led to the formation of a mixture of products. GC-MS analysis indicated the formation of five different compounds with two M^+ signals corresponding to 230 (**7-9**) and 288/290 (**10**, **11**) in a ratio of 2:4:3:1:2, respectively in high yield (80%). After column chromatographic separations on silica gel containing 1% $AgNO_3$, the compounds were characterized separately. (Scheme 2).



Scheme 2

The ^{1}H NMR spectrum of **7** indicated the presence of four sets of signals: a multiplet for the protons of the phenyl ring at 7.32-7.22 ppm, a doublet at 6.81 ppm ($^{3}J_{HF}$ = 9.0 Hz, H_7) for the aromatic proton H_7 along with a triplet at 2.85 ppm (^{3}J = 7.4 Hz, 4H) and a quintet at 2.06 ppm (J= 7.7 Hz, 2H). The magnitude of the coupling constant ($^{3}J_{HF}$ = 9.0 Hz) suggested that this splitting arises from the interaction of the proton with a fluorine atom, which is located in the ortho position.[12] Furthermore, the ^{19}F-NMR spectrum has shown the presence of two fluorine atoms resonating at -118.8 and -117.6 ppm, which are in the range of the chemical shifts of the aromatic fluorine atoms, giving rise in turn to doublets with a coupling constant of $^{4}J_{FF}$ = 5.6 Hz in which its magnitude clearly suggests that the two fluorine atoms are located in meta position (Table 1).

Table 1. ^{19}F-NMR chemical shifts (in ppm) and coupling constants (in Hz) with spin multiplities for fluoro-indane derivatives in $CDCl_3$

Compound	F_a	F_b	J_{FF}
7	-117.6 (d)	-118.8 (dd)	^{4}J= 5.6
8	-140.6 (dd)	-146.2 (dd)	^{3}J= 20.3
9	-115.6 (t)	-117.4 (t)	^{4}J= 7.0
10	-113.3 (d)	--	--
11	-119.3 (d)	--	--

The comprehensive evidence for the structure **7** came from the proton-decoupled ^{13}C-NMR spectrum in conjunction with the 2D-NMR (COSY, DEPT-135, HMQC and HMBC) experiments. The aromatic carbon C_7 with an attached proton (δ 107.8), as shown by the DEPT experiment, is split into a doublet of doublets ($^{2}J_{CF}$ = 23.5 and $^{4}J_{CF}$ = 3.6 Hz). The magnitudes of these coupling constants indicate that this carbon (C_7) is ortho to a one fluorine atom and para to the other. The carbon holding phenyl ring resonates at 116.3 ppm as triplets with a coupling constant ($^{2}J_{CF}$ = 19.0 Hz) which strongly suggests the presence of two fluorine atoms in the ortho position of this carbon. Similar C-F coupling constant arguments can be made for the doublet of doublets at δ 126.0 (C_{3a}, J_{CF} = 19.6 and 2.8 Hz, ortho to one fluorine and para to the other) and

146.8 (C_{7a}, J_{CF} = 9.5 and 7.8 Hz, meta to both fluorine's). The carbon atoms bonded to the fluorine's appear as a doublet of doublets centered at δ 159.5 ($^1J_{CF}$ = 245.1 and 5.7 Hz), and δ 156.3 ($^1J_{CF}$ = 247.4 and 7.8 Hz). The magnitude of the smaller C-F coupling constant in these carbon resonances unambiguously indicates that the two fluorine atoms are meta to one another.[12] When taken together, these data firmly establish the structure of the previously unknown compound **7**.

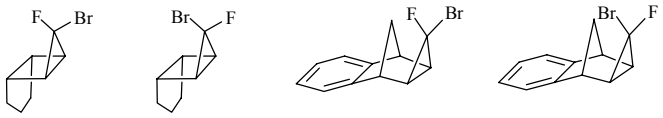
In a similar vein, the other products **8-11** were also characterized in which the spectroscopic data are given in the experimental section. The ortho position of the fluorine atoms in **8** and the meta position of fluorine atoms in **9** were easily determined from the coupling constants $^3J_{FF}$ = 20.3 Hz for **8** and $^4J_{FF}$ = 7.0 Hz for **9**, respectively. To the best of our knowledge, these are the first examples of fluorine-substituted phenylindanes.

The observation of such products as **7-11** led us to propose a complex mechanistic scenario for the addition of bromofluorocarbene to cyclobutene **4**, which presumably involves the initial formation of *gem*-bromofluoro cyclopropane **12**. The bromofluoro carbene can approach the double bond in **4** in two different ways, which in turn leads to the formation of **12a** (*endo*-fluoro-*exo*-bromo) and **12b** (*endo*-bromo-*exo*-fluoro). As **12** is formed, it undergoes electrocyclic ring-expansion in order to decrease the accommodated strain arising from the fusion of three small rings (*three*-, *four*-, and *five*-membered rings, respectively) (Schemes 3, 4 and 5).

12a **12b**

Figure 2

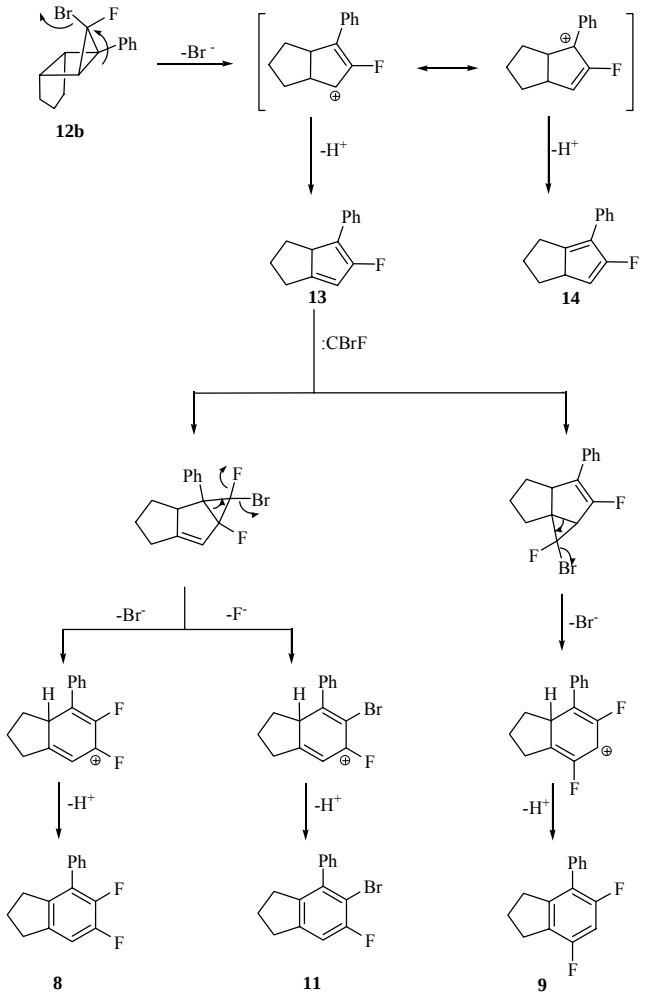
The formation of **12b** where the bulky bromine atom is in the *endo*-position cannot be excluded due to the steric reasons (Figure 2). Recently, we have clearly shown that the bromofluoro carbene adds to benzonorbornadiene and bicyclohept-6-ene and forms the isomeric addition products **3a/3b** and **2a/2b**, respectively (Scheme 3). Furthermore, we noticed that the isomers **3b** and **2b** underwent a ring-opening reaction, whereas the isomers **3a** and **2a** were stable under the given reaction conditions. Therefore, the formation of **2b** and **3b** also strongly supports the formation of the isomeric addition product **12b**.



3a **3b** **2a** **2b**

Figure 3

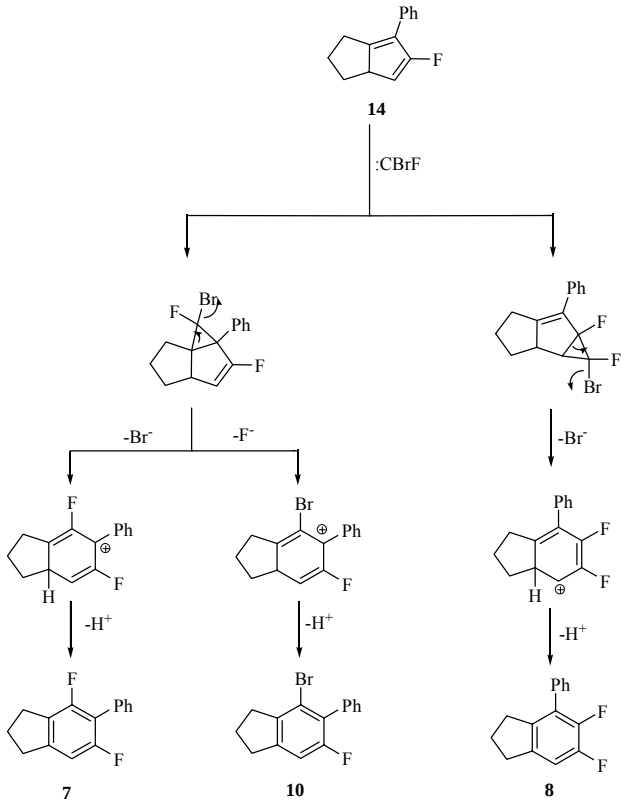
The ring opening reaction has been rationalized in terms of orbital symmetry conservation.[13] It has been well established that the departing halide is the one that is in the *endo*-position. According to the Woodward-Hoffmann rules, the isomer **12b** (Figure 2) should easily undergo a ring opening reaction, whereas the isomer **12a**, where the bromine atom is in the *exo*-position, should be stable.[4-6] However, careful examination of the reaction mixture did not reveal the presence of the isomer **12a**. Therefore, we assume that the isomer **12a** also easily undergoes ring-opening reaction. Recently, Lewis *et al.*[6b] have demonstrated that the product obtained by the addition of difluorocarbene to 1,2-diphenylcyclobutene can easily undergo a ring opening reaction in spite of the fact that the departing halogen is a fluorine atom. We assume that the phenyl ring attached to the cyclopropane ring plays an important role in the ring opening reaction of **12a**.



Scheme 3

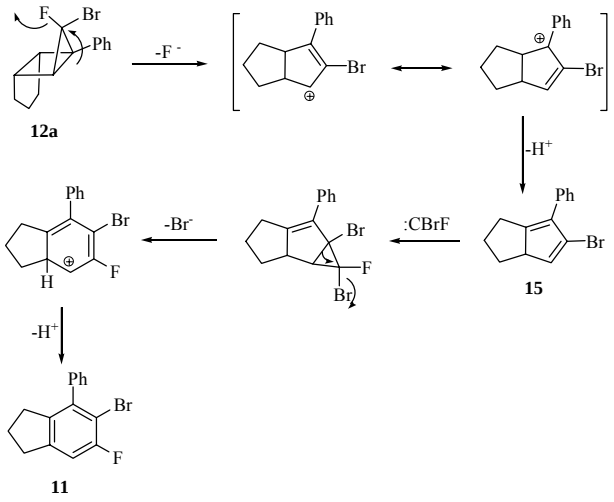
Once the ring-expansion of **12b** occurred, the two cationic intermediates formed could provide the cyclopentadienes **13** and **14** by the direct elimination of a proton (Scheme 3). After

the formation of **13** and **14**, the second addition of bromofluorocarbene might take place with two alternate paths for each, due to the presence of two unequal double bonds. The proposed mechanism with alternate paths is depicted for each case (Schemes 3 and 4). It is obvious that the presence of the cyclopentadiene **13** alone in the reaction can explain the formation of **8**, **9** and **11** but not **7** and **10**. In an analogy, the formation of **7**, **8**, and **10** can be explained by the addition of bromofluoro carbene to the cyclopentadiene derivative **14** as depicted in Scheme 4. Furthermore, it is reasonable that cyclopentadienes such as **13** and **14** under reaction conditions are prone to undergo fast intramolecular 1,5-H-shifts before bromofluorocarbene attack takes place as it would further complicate the reaction mechanism.



Scheme 4

The *endo*-fluoro-*exo*-bromo isomer **12a** can easily undergo a ring-opening reaction where the departing halide is a fluorine atom. We assume that the phenyl substituent aids in fluoride ion loss. The second addition of bromofluorocarbene to the formed cyclopentadiene derivative **15** will result in the formation of **11** (Scheme 5).



Scheme 5

Conclusions

In summary, the addition of bromofluorocarbene to cyclobutene **4** resulted in the formation of fluoro-indanes such as **7-11** by ring expansion in one step where *gem*-bromofluoro cyclopropane **12** is set as a reactive intermediate. Efforts to investigate the scope and limitations for the existence of bromofluorocyclopropanes en route to strained cyclic allenes are currently underway in our laboratory.

Experimental Section

General Procedures. Infrared spectra were recorded on a Mattson model 1000 FT-IR spectrometer. ^{1}H-, ^{13}C- and ^{19}F-NMR spectra were recorded on 400, 100 and 376.3 MHz spectrometers (Bruker), respectively. Mass spectra (electron impact) were recorded at 70 eV. Column chromatography was performed on silica gel (60-200 mesh) from Merck Company. TLC was carried out on Merck 0.2 mm silica gel 60 F254 analytical aluminum plates.

Compounds & characterization

Synthesis of 4 and 6. A solution of 7.5 g (40 mmol) alcohol **5** and 0.7 g (4 mmol) *p*-TsOH in 100 mL toluene was heated under reflux in a Dean-Stark trap, which was attached to a condenser. After 16 h the flask was allowed to cool to room temperature. The solution was washed first with $NaHCO_3$ solution, and then with brine, dried over $CaCl_2$. After evaporation of the solvent the residue was filtered on a silica gel (50 g) column eluting with hexane to give 4.1 g (24 mmol, yellowish liquid) of **4** and 1.0 g (6 mmol, colorless liquid) of **6** in a total yield of 75%.

6-Phenylbicyclo[3.2.0]hept-6-ene (4).[8] Colorless liquid (70 °C, bad temperature, 0.1 Torr[8b]), ^{1}H-NMR (400 MHz) δ 7.17-6.99 (5H, m, aromatic), 5.95 (1H, bs, olefinic), 3.33-3.31 (1H, m, CH), 2.99-2.97 (1H, m, CH), 1.63-1.09 (6H, m); ^{13}C-NMR (100.55 MHz) δ 146.2, 134.1, 128.4, 128.0, 127.4, 124.8, 46.2, 44.0, 26.9, 26.3, 23.8.

1-Phenylbicyclo[4.1.0]hept-2-ene (6).[8a] Colorless liquid, ^{1}H-NMR (400 MHz) δ 7.21-7.17 (4H, m, aromatic), 7.10-7.04 (1H, m, aromatic), 6.08 (1H, dd, A-part of AB system, *J*= 10.0-2.2 Hz, H-2), 5.48 (1H, ddd, B-part of AB system, *J* = 10.0, 6.4 and 2.2 Hz, H-3), 2.02-1.92 (2H, m, methylenic), 1.79-1.67 (2H, m, methylenic), 1.44-1.42 (1H, m, H-6), 1.27 (1H, dd, *J*= 8.5 and 4.9 Hz, H-7), 1.04 (1H, bt, *J*= 4.9 Hz, 1H); ^{13}C-NMR (100.55 MHz) δ 146.5 (s), 133.0 (d, $^1J_{CH}$ = 151.4 Hz), 128.7 (d, $^1J_{CH}$ = 158.0 Hz), 127.5 (d, $^1J_{CH}$ = 156.0 Hz), 126.0 (d, $^1J_{CH}$ = 151.7 Hz), 123.2 (d, $^1J_{CH}$ = 157.3 Hz), 25.6 (d, $^1J_{CH}$ = 158.4 Hz), 24.3, 20.8 (t, $^1J_{CH}$ = 127.6 Hz), 19.0 (t, $^1J_{CH}$ = 126.2 Hz), 18.4 (t, $^1J_{CH}$ = 160.4 Hz); MS (m/z, relative intensity): 169 (M^+-H, 65), 153 (100), 141 (90), 127 (65), 114 (45), 101 (15), 90 (30), 76 (45), 50 (35).

Bromofluorocarbene Addition to 4. To a magnetically stirring solution of 1.0 g (6 mmol) olefin **4**, 2.8 g (14.8 mmol) $CHBr_2F$ and 0.25 g (1 mmol) $PhCH_2NEt_3Cl$ in 100 ml CH_2Cl_2, a solution of 2.2 g (54 mmol) NaOH dissolved in 2.5 mL water was dropwise added at -5 °C over a period of 2 h. After stirring for an additional 8 h at room temperature, the reaction mixture was diluted with 250 mL water and extracted with CH_2Cl_2 (3 x 100 mL), dried over $MgSO_4$, and the solvent was removed under reduced pressure. Repeated column chromatography of the residue (1% $AgNO_3$-silica gel, 100 g) with hexane as eluant gave compounds **7** (0.20 g, 13%, colorless liquid), **8** (0.40 g, 27%, colorless liquid), **9** (0.30 g, 20%, colorless liquid), **10** (0.10 g, 7%, colorless liquid), and **11** (0.20 g, 13%, colorless liquid).

4,6-Difluoro-5-phenylindane (7). Colorless liquid, ^{1}H-NMR (400 MHz) δ 7.32-7.30 (4H, m, aromatic), 7. 26-7.23 (1H, m, aromatic) 6.81 (1H, d, $^3J_{HF}$= 9.0 Hz, H-7), 2.85 (4H, *t*, *J*= 7.4 Hz, H-1 and H-3), 2.06 (2H, *J*=7.4 Hz, H-2); ^{13}C-NMR (The multiplicities of the carbon resonances were determined from the DEPT spectra) (100.55 MHz, $CDCl_3$) δ 159.5 (dd, $^1J_{CF}$ = 245.1 Hz, $^3J_{CF}$ = 5.7 Hz, C-4), 156.3 (dd, $^1J_{CF}$ = 247.4 Hz, $^3J_{CF}$ = 7.8 Hz, C-6), 146.8 (dd, $^3J_{CF}$ = 9.5 Hz, $^3J_{CF}$ = 7.8 Hz, C-7a), 130.8 (d, C-$2_{arom.}$), 130.4 (s, C-$1_{arom.}$), 128.5 (d, C-3_{arom}), 128.1 (d, C-4_{arom}), 126.0 (dd, $^2J_{CF}$= 19.6 Hz, $^4J_{CF}$= 2.8 Hz, C-3a), 116.3 (t, $^2J_{CF}$ =19.0 Hz, C-5), 107.8 (dd, $^2J_{CF}$ =23.5 Hz, $^4J_{CF}$= 3.6 Hz, C-7), 33.8 (t, C-1), 29.0 (t, C-3), 25.8 (t, C-2); ^{19}F-NMR (376.2 MHz, $CDCl_3$) δ -117.6 (d, $^4J_{FF}$ = 5.6 Hz, F-C-6), -118.8 (t, $^4J_{FF}$ = $^3J_{HF}$ 7.1 Hz, F-C-4); MS (m/z, relative intensity): 230 (M^+, 70), 152 (25), 132 (10), 100 (10), 76 (10), 50 (7). IR ($CHCl_3$, cm^{-1}): 3084 (sh), 3056 (sh), 3021 (m), 2951 (s), 2944 (sh), 2909 (sh), 2853 (s), 2832 (sh), 1644 (m), 1567 (m), 1462 (s), 1420 (s), 1329 (m), 1266 (w) , 1106v(m) , 1022 (m), 847 (m) , 763 (m) , 686 (m), 560 (w). Anal. Calcd. for $C_{15}H_{12}F_2$: C, 78.24; H, 5.25. Found: C, 77.85; H, 5.11.

5,6-Difluoro-4-phenylindane (8). Colorless liquid, ^{1}H-NMR (400 MHz) δ 7.46-7.35 (5H, m, aromatic), 6.88 (1H, dd, $^3J_{HF}$ = 9.4 Hz, $^4J_{HF}$ = 7.1 Hz, H-7), 2.95 (2H, t, *J*= 7.3 Hz), 2.80 (2H, t, *J* =7.3 Hz), 2.08 (2H, qui, *J*= 7.3 Hz); ^{13}C-NMR (100 MHz) δ 150.1 (dd, $^1J_{CF}$ = 245.0 Hz, $^2J_{CF}$ = 14.5 Hz, C-5), 146.9 (dd, $^1J_{CF}$= 243.7 Hz, $^2J_{CF}$= 13.7 Hz, C-6), 139.4 (dd, $^3J_{CF}$= 6.0 Hz, $^4J_{CF}$ = 3.5 Hz, C-3a), 138.7 (bs, C-7a), 134.4 (s, C-$1_{arom.}$), 130.0 (d), 128.6 (d), 127.8 (d), 127.7 (bd,

$^2J_{CF}$= 10.4 Hz, C-4), 111.9 (d, $^2J_{CF}$ =17.5 Hz, C -7), 33.4 (C-1), 32.8 (C-3), 26.3 (C-2); ^{19}F-NMR (376.3 MHz, $CDCl_3$) δ -140.6 (dd, $^3J_{FF}$ = 20.3 Hz, $^3J_{FH}$ = 9.8 Hz F-C -6), -146.2 (dd, $^3J_{FF}$ = 20.3 Hz, $^3J_{FH}$ = 7.2 Hz F-C-5); MS (m/z, relative intensity): 230 (M^+, 95), 152 (50), 132 (12), 100 (15), 76 (8), 62 (5), 50 (10). IR ($CHCl_3$, cm^{-1}): 3056 (w), 2958 (s), 2951 (s), 2846 (m), 1700 (w), 1616 (s) , 1476 (vs), 1441 (s), 1343 (s), 1203 (sh), 1238 (w), 1126 (m), 1071 (w), 1029 (w), 868 (m), 770 (s), 700 (s), 644 (w), 574 (w). Anal. Calcd. for $C_{15}H_{12}F_2$: C, 78.24; H, 5.25. Found: C, 78.51; H, 5.09.

5,7-Difluoro-4-phenylindane (9). Colorless liquid, ^{1}H-NMR (400 MHz) δ 7.36-7.22 (5H, m, aromatic), 6.62 (1H, t, $^3J_{HF}$= 9.2 Hz, H-6), 2.87 (2H, t, *J*=7.4 Hz, H-1), 2.75 (2H, t, *J*=7.4 Hz, H-3), 2.01 (2H, qui, *J*= 7.4 Hz, 2H); ^{13}C-NMR (100 MHz) δ 159.1 (dd, $^1J_{CF}$= 244.9 Hz, $^3J_{CF}$= 10.4 Hz, C_5), 158.1 (dd, $^1J_{CF}$ =246.7 Hz, $^3J_{CF}$= 12.7 Hz, C-7), 147.7 (t, $^3J_{CF}$ = 5.2 Hz, C-3a), 134.6 (s) (C-1_{arom}), 129.8 (d), 128.5 (d), 128.1 (d) , 125.7 (dd, $^2J_{CF}$= 14.9, $^4J_{CF}$= 3.3 Hz, C-7a), 122.4 (dd, $^2J_{CF}$= 16.2, $^4J_{CF}$= 3.1 Hz, C-4), 102.1 (dd, $^2J_{CF}$= 27.5 and 24.7 Hz, C-6), 33.6 (t, C-3), 29.8 (t, C-1), 26.0 (t, C-2); ^{19}F-NMR (376.3 MHz, $CDCl_3$) δ -115.6 (t, $^3J_{FH}$=$^4J_{FF}$ =7.0 Hz), -117.4 (br.t, $^3J_{FH}$=$^4J_{FF}$ = 7.0 Hz); MS (m/z, relative intensity): 230 (M^+, 80), 152 (25), 132 (8), 100 (10), 76 (5), 62 (3), 50 (7). IR ($CHCl_3$, cm^{-1}): 2944 (sh), 2923 (m), 2846 (w), 1721 (w), 1658 (w) , 1609 (w) , 1455 (w), 1371 (w), 1287 (w) , 1217 (m), 1113 (w), 882 (w), 763 (vs), 707 (w) , 679 (w). Anal. Calcd. for $C_{15}H_{12}F_2$: C, 78.24; H, 5.25. Found: C, 78.15; H, 5.13.

4-Bromo-6-fluoro-5-phenylindane (10). Colorless liquid, ^{1}H-NMR (400 MHz) δ 7.36-7.27 (3H, m, aromatic), 7.19 (2H, bd, *J*= 7.9 Hz, aromatic), 6.87 (1H, d, $^3J_{HF}$= 8.7 Hz, H-7), 2.99 (2H, t, *J*= 7.5 Hz, -CH_2-), 2.90 (2H, t, *J*= 7.5 Hz, -CH_2-), 2.08 (2H, qui, *J*= 7.5 Hz, H-2); ^{13}C-NMR (100.55 MHz) δ 159.3 (d, $^1J_{CF}$= 245.4 Hz, C-6), 145.5 (d, $^3J_{CF}$ = 8.5 Hz, C-7a), 140.9 (d, $^4J_{CF}$= 2.8 Hz, C-3a), 135.4 (s, C-$1_{arom.}$), 130.6 (d, C-$2_{arom.}$), 128.5 (d, $^2J_{CF}$= 26.9 Hz, C-5), 128.3 (d, C-$3_{arom.}$), 128.2 (4, C-$4_{arom.}$), 121.6 (d, $^3J_{CF}$= 3.9 Hz, C-4), 111.0 (d, $^2J_{CF}$ = 24.0 Hz, C-7), 35.1 (t, C-1), 34.6 (t, C-3), 24.8 (t, C-2); ^{19}F-NMR (376.3 MHz, $CDCl_3$) δ -113.3 (d, $^3J_{FH}$= 24.0 F-C-6); MS (m/z, relative intensity): 290/288 (M^+, 95), 210 (30), 195 (70), 182 (55), 168 (10), 132 (30), 103 (25), 91 (25), 50 (10). IR ($CHCl_3$, cm^{-1}): 2958 (sh), 2951 (sh), 2916 (m) , 2846 (w), 1658 (w) , 1609 (m), 1399 (w), 1217 (m), 1113 (w), 1092 (w), 819 (w), 777 (vs), 651 (w). Anal. Calcd. for $C_{15}H_{12}BrF$: C, 61.88; H, 4.15. Found: C, 61.43; H, 4.06.

5-Bromo-6-fluoro-4-phenylindane (11). Colorless liquid, ^{1}H-NMR (400 MHz) δ 7.34-7.22 (5H, m, aromatic), 7.07 (1H, d, $^2J_{HF}$= 9.2 Hz, H-7), 2.89 (t, *J*=7.4 Hz, H-1), 2.85 (2H, t, *J*=7.4 Hz, H-3), 1.98 (2H, qui, *J*=7.4 Hz, H-2); ^{13}C-NMR (100 MHz) δ 158.8 (d, $^1J_{CF}$ = 247.0 Hz, C-6), 146.0 (s, C-3a), 140.3 (s, C-7a), 134.4 (s, C-1_{arom}), 129.7 (d, C-3_{arom}), 128.5 (d,C-2_{arom}), 127.9 (d, C-4_{arom}), 125.6 (d, $^2J_{CF}$= 16.3 Hz, C-5), 118.3 (d, $^3J_{CF}$= 10.7 Hz, C-4), 117.4 (d, $^2J_{CF}$ = 26.9 Hz, C-7), 34.5 (t, C-3), 34.4 (d, $^4J_{CF}$= 2.9 Hz, C-1), 25.2 (t, C-2); ^{19}F-NMR (376.3 MHz, $CDCl_3$) δ -119.3 (d, $^3J_{FH}$= 9.4 Hz); MS (m/z, relative intensity): 290/288 (M^+, 85), 210 (45), 195 (65), 182 (55), 132 (40), 103 (30), 91 (35), 76 (20), 50 (15), 43 (50). IR ($CHCl_3$, cm^{-1}): 2959 (m), 2944 (m), 2916 (s), 2853 (m), 1679 (m), 1623 (s), 1455 (m) , 1406 (w), 1371 (w), 1217 (w), 1126 (m), 1092 (w), 770 (vs), 707 (w), 644 (w), 602 (w). Anal. Calcd. for $C_{15}H_{12}BrF$: C, 61.88; H, 4.15. Found: C, 61.47; H, 4.29.

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