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CuCl-catalyzed isomerization of *gem*-chlorofluorocyclopropanes into chlorofluoroalkenes

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General procedure for the synthesis of *gem*-chlorofluorocyclopropanes. The starting *gem*-chlorofluorocyclopropanes were synthesized in accordance with a published procedure[1] by the addition of chlorofluorocarbene, which was generated from dichlorofluoromethane under the action of KOH under the conditions of phase-transfer catalysis, to corresponding alkenes. 130 g of a 50% aqueous solution of KOH (1.2 mol) were added to a solution of 0.5 mol of an alkene, 0.7 mol of $CHCl_2F$ and 1.0 g of $BnEt_3NCl$ in 100 ml of CH_2Cl_2 cooled to –5 °C with intense stirring for 1 h keeping the temperature of the reaction mixture in a range of 0 − +5 °C; thereafter, the reaction mixture was additionally stirred for 8 h and diluted with water. The organic product was washed with water and dried with $CaCl_2$, and *gem*-chlorofluorocyclopropanes were separated by distillation.

1-Chloro-1-fluoro-2-phenylcyclopropane 1[2] (*syn* : *anti* = 58:42), yield 81%, bp 70−71 °C / 6 Torr.

For *syn*-**1**. ^{1}H NMR ($CDCl_3$, 300.1 MHz) δ (ppm): 7.45—7.25 (m, 5H, arom.), 2.93 (ddd, 17.0 Hz, 11.6 Hz, 8.4 Hz, 1H, cycloprop.), 2.10—1.50 (m, 2H, cycloprop.); ^{19}F NMR ($CDCl_3$, 282.4 MHz) δ (ppm): –129.1 (ddd, 17.0 Hz, 17.0 Hz, 6.4 Hz). For *anti*-**1**. ^{1}H NMR ($CDCl_3$, 300.1 MHz) δ (ppm): 7.45—7.25 (m, 5H, arom.), 2.76 (m, 1H, cycloprop.), 2.10—1.50 (m, 2H, cycloprop.); ^{19}F NMR ($CDCl_3$, 282.4 MHz) δ (ppm): –149.5 (br. dd, 14.8 Hz, 8.5 Hz).

1-Chloro-1-fluoro-2,2-dimethylcyclopropane 4[3]. Yield 88%, bp 80−81 °C.

^{1}H NMR ($CDCl_3$, 200.1 MHz) δ (ppm): 1.27 (s, 3H, CH_3), 1.26 (s, 3H, CH_3), 1.21 (dd, 17.2 Hz, 7.0 Hz, 1H, cycloprop.), 0.97 (dd, 7.0 Hz, 7.0 Hz, 1H, cycloprop.); ^{19}F NMR ($CDCl_3$, 188.3 MHz) δ (ppm): –141.3 (dd, 17.2 Hz, 7.0 Hz); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ (ppm): 99.2 (d, 292 Hz, CFCl), 27.6 (d, 10 Hz, CH_2), 24.8 (d, 10 Hz, C), 22.6 (d, 1 Hz, CH_3), 19.1 (d, 9 Hz, CH_3); mass spectrum (*m*/*z*, %): 122, 124 (M^+, 9, 3), 107, 109 (M^+–CH_3, 65, 20), 87 (M^+-Cl, 100), 71 (29), 59 (37).

1-Chloro-1-fluoro-*cis*-2,3-dimethylcyclopropane 7[4] (*syn* : *anti* = 68:32), yield 74%, bp 91−95 °C.

^{1}H NMR ($CDCl_3$, 200.1 MHz) δ (ppm): 1.70—1.40 (m, 2H, 2CH, both isomers), 1.15—1.10 (m, 6H, $2CH_3$, both isomers); ^{19}F NMR ($CDCl_3$, 188.3 MHz) δ (ppm): –126.2 (t, 19.3 Hz, *syn*-**7**), -163.9 (br. s, *anti*-**7**); mass spectrum (*m*/*z*, %) for *syn*-**7**: 122, 124 (M^+, 13, 5), 107, 109 (M^+–CH_3, 53, 18), 87 (M^+-Cl, 100), 71 (30), 59 (47); mass spectrum (*m*/*z*, %) for *anti*-**7**: 122, 124 (M^+, 15, 5), 107, 109 (M^+–CH_3, 32, 12), 87 (M^+-Cl, 100), 71 (22), 59 (42).

7-Chloro-7-fluorobicyclo[4.1.0]heptane 9,[5] (*endo* : *exo* = 65:35), yield 62%, bp 76−77 °C / 52 Torr.

^{1}H NMR ($CDCl_3$, 300.1 MHz) δ (ppm): (a mixture of *endo* and *exo* isomers): 2.00—1.40 (m, 6H), 1.40—1.15 (m, 4H); ^{19}F NMR ($CDCl_3$, 282.4 MHz) -124.4 (t, 19.1 Hz, *endo*-Cl-**9**), -158.3 (br. s, *exo*-Cl-**9**).

1-Chloro-1-fluoro-2-vinylcyclopropane 12a,[1] (*syn* : *anti* = 62:38), yield 63%, bp 88−90 °C.

For *syn*-**12a**: ^{1}H NMR ($CDCl_3$, 200.1 MHz) δ (ppm): 5.62—5.43 (m, 1H, H_2C=CH–), 5.37—5.18 (m, 2H, H_2C=CH–), 2.42—2.08 (m, 1H, CH-cycloprop.), 1.79 (m, 1H, CH_2-cycloprop.), 1.22 (m, 1H, CH_2-cycloprop.); ^{19}F NMR ($CDCl_3$, 188.3 MHz) δ (ppm): –130.2 (br. ddd, 17.0 Hz, 17.0 Hz, 7.3 Hz); mass spectrum (*m*/*z*, %): 120, 122 (M^+, 6, 2), 85 (M^+–Cl, 100), 65 (M^+–Cl–HF, 31). For *anti*-**12a**: ^{1}H NMR ($CDCl_3$, 200.1 MHz) δ (ppm): 5.62—5.43 (m, 1H, H_2C=CH–), 5.37—5.18 (m, 2H, H_2C=CH–), 2.42—2.08 (m, 1H, CH-cycloprop.), 1.651.73 (m, 2H, CH_2-cycloprop.); ^{19}F NMR ($CDCl_3$, 188.3 MHz) δ (ppm): –147.7 (br. dd, 16.4 Hz, 7.8 Hz); mass spectrum (*m*/*z*, %): 120, 122 (M^+, 9, 3), 85 (M^+–Cl, 100), 65 (M^+–Cl–HF, 40).

1-Chloro-1-fluoro-2-methyl-2-vinylcyclopropane 12b,[1] (*syn* : *anti* = 50:50), yield 85%, bp 105−108 °C.

For the mixture of *syn* and *anti*-isomers: ^{1}H NMR ($CDCl_3$, 200.1 MHz) δ (ppm): 5.82—5.64 (m, 1H, H_2C=CH–), 5.32—5.11 (m, 2H, H_2C=CH–), 1.39—1.37 (m, 3H, CH_3), 1.68—1.20 (m, 2H, cycloprop.); ^{19}F NMR ($CDCl_3$, 188.3 MHz) δ (ppm): –138.7 (ddq, 15.6 Hz, 8.1 Hz, 1.8 Hz), –139.2 (ddq, 16.4 Hz, 7.4 Hz, 2.0 Hz); mass spectrum (*m*/*z*, %): 99 (M^+–Cl, 18), 80 (M^+–Cl–F, 32), 79 (M^+–Cl–HF, 68), 77 (22), 51 (45), 27 (100).

2-Chloro-2-fluoro-1,1'-bi(cyclopropyl) 15, (*syn* : *anti* = 48:52), yield 54%, bp 86−87 °C/ 125 Torr.

For the mixture of *syn* and *anti*-isomers: ^{1}H NMR ($CDCl_3$, 200.1 MHz) δ (ppm): 1.62—1.73 (m, 4H), 0.71—0.42 (m, 2H), 0.39—0.10 (m, 2H); ^{19}F NMR ($CDCl_3$, 188.3 MHz) δ (ppm): –129.4 (ddd, 17.1 Hz, 17.1 Hz, 5.8 Hz, *syn*-**15**), –149.9 (m, *anti*-**15**).

General procedure for the isomerization of *gem*-chlorofluorocyclopropanes

Method A. A mixture of 2−4 mmol of *gem*-chlorofluorocyclopropane and 0.1−2 mmol of CuCl in 2 ml of MeCN was stirred in an atmosphere of argon at 80 °C for 7−90 h in different experiments. The reaction was monitored by GLC. After completion of the reaction, the reaction mixture was diluted with 20 ml of CH_2Cl_2, washed with water (3 x 50 ml) and dried with Na_2SO_4. The solvent was distilled off, and the residue was analyzed by GLC, NMR spectroscopy, and GS/MS.

Method B. A mixture of 40−80 mmol of cyclopropane, 4−8 mmol of CuCl, 4−8 mmol of LiCl and 20 ml of MeCN was heated in an atmosphere of argon in a glass liner in a steel autoclave at 80 °C for 24−96 h. The reaction was monitored by GLC. After completion of the reaction, the reaction mixture was diluted with 50 ml of CH_2Cl_2, washed with water (3 x 50 ml) and dried with Na_2SO_4. The solvent was distilled off using a rotary evaporator or by fraction distillation at atmospheric pressure, and the residue was distilled.

Isomerization of 1-chloro-1-fluoro-2-phenylcyclopropane 1

According to method A, a mixture of 347 mg (2.0 mmol) of **1**, 100 mg (1.0 mmol) of CuCl and 2.0 ml of MeCN was stirred at 80 °C for 50 h. After separation, 342 mg of a mixture containing 65% *Z*-**2**, 33% *E*-**2** and 1% **3** was obtained (according to GLC and ^{1}H and ^{19}F NMR-spectroscopic data).

Analogously, the experiments were performed at different amounts of CuCl in the presence of LiCl in MeCN, diglyme and dioxane.

According to method B, a mixture of 6.82 g (40 mmol) of **1**, 402 mg (4.1 mmol) of CuCl, 170 mg (4.0 mmol) of LiCl and 20 ml of MeCN was heated at 80−90 °C for 48 h. After treatment, 6.68 g of a mixture of (*Z*)- and (*E*)-3-chloro-2-fluoro-1-phenylpropenes **2** (*Z* / *E* = 7.1 : 1) as a colorless liquid were obtained (yield, 98%). 4.36 g of *Z*-**2** (yield, 64%; *Z*/*E* > 99, bp 94−95 °C / 6 Torr) were separated by distillation.

(*Z*)-3-Chloro-2-fluoro-1-phenylpropene *Z*-2

^{1}H NMR ($CDCl_3$, 200.1 MHz) δ (ppm): 7.75—7.25 (m, 5H, arom.), 5.92 (d, 36.4 Hz, 1H, CH=), 4.29 (d, 18.7 Hz, 2H, CH_2Cl); ^{19}F NMR ($CDCl_3$, 188.3 MHz) δ (ppm): –109.5 (dt, 36.4 Hz, 18.7 Hz); mass spectrum (*m*/*z*, %): 170, 172 (M^+, 40, 14), 135 (M^+–Cl, 100), 133 (31), 115 (55).

(*E*)-3-Chloro -2-fluoro-1-phenylpropene *E*-2

^{1}H NMR ($CDCl_3$, 200.1 MHz) δ (ppm): 7.75—7.25 (m, 5H, arom.), 6.58 (d, 18.7 Hz, 1H, CH=), 4.38 (d, 21.8 Hz, 2H, CH_2Cl); ^{19}F NMR ($CDCl_3$, 188.3 MHz) δ (ppm): –105.1 (td, 21.8 Hz, 18.7 Hz); mass spectrum (*m*/*z*, %): 170, 172 (M^+, 41, 14), 135 (M^+–Cl, 100), 133 (34), 115 (58).

3-Chloro-2-fluoro-3-phenylpropene 3

^{1}H NMR ($CDCl_3$, 200.1 MHz) δ (ppm): 7.75—7.25 (m, 5H, arom.), 5.58 (d, 13.3 Hz, 1H, CHCl), 4.97 (dd, 16.0 Hz, 3.6 Hz, 1H, CH_2), 4.81 (dd, 46.6 Hz, 3.6 Hz, 1H, CH_2); ^{19}F NMR ($CDCl_3$, 188.3 MHz) δ (ppm): –103.8 (ddd, 46.6 Hz, 16.0 Hz, 13.3 Hz); mass spectrum (*m*/*z*, %): 170, 172 (M^+, 15, 5), 135 (M^+–Cl, 100), 133 (32), 115 (58).

Isomerization of 1-chloro-1-fluoro-2,2-dimethylcyclopropane 4

According to method B, a mixture of 19.6 g (160 mmol) of **4**, 795 mg (8.0 mmol) of CuCl, 340 mg (8.0 mmol) of LiCl and 40 ml of MeCN was heated at 80−90 °C for 36 h. After treatment, 18.0 g of a mixture containing 75% **5** and 25% **6**, which was further separated by fraction distillation, were obtained. 3.83 g of 3-chloro-2-fluoro-3-methylbut-1-ene **6** (bp 88−89 °C; yield, 20%) and 12.2 g of 1-chloro-2-fluoro-3-methylbut-2-ene **5** (bp 66−67 °C / 110 Torr; yield, 62%) were obtained.

1-Chloro-2-fluoro-3-methylbut-2-ene 5

^{1}H NMR ($CDCl_3$, 200.1 MHz) δ (ppm): 4.20 (d, 22.4 Hz, 2H, CH_2Cl), 1.72 (s, 3H, CH_3), 1.70 (s, 3H, CH_3); ^{19}F NMR ($CDCl_3$, 188.3 MHz) δ (ppm): –117.2 (t, 22.4 Hz); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ (ppm): 149.3 (d, 239 Hz, CF=), 115.0 (d, 17 Hz, Me_2C=), 39.0 (d, 34 Hz, CH_2Cl), 17.5 (d, 4 Hz, CH_3), 15.9 (d, 7 Hz, CH_3); mass spectrum (*m*/*z*, %): 122, 124 (M^+, 32, 12), 87 (M^+–Cl, 100), 59 (50), 41 (49).

3-Chloro-2-fluoro-3-methylbut-1-ene 6

^{1}H NMR ($CDCl_3$, 200.1 MHz) δ (ppm): 4.66 (dd, 16.3 Hz, 3.3 Hz, 1H, $=CH_2$), 4.65 (dd, 48.2 Hz, 3.3 Hz, 1H, $=CH_2$), 1.75 (d, 1.0 Hz, 6H, $2CH_3$); ^{19}F NMR ($CDCl_3$, 188.3 MHz) δ (ppm): –105.6 (br. dd, 48.2 Hz, 16.3 Hz); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ (ppm): 167.0 (d, 259 Hz, CF=), 89.6 (d, 21 Hz, $=CH_2$), 64.3 (d, 28 Hz, Me_2CCl), 29.9 (s, $2CH_3$); mass spectrum (*m*/*z*, %): 122, 124 (M^+, 14, 4), 107, 109 (M^+–CH_3, 22, 8), 87 (M^+–Cl, 100), 59 (39), 41 (46).

Isomerization of 1-chloro-1-fluoro-*cis*-2,3-dimethylcyclopropane 7

According to method B, a mixture of 9.80 g (80 mmol) of **7**, 396 mg (4.0 mmol) of CuCl, 206 mg (4.9 mmol) of LiCl and 20 ml of MeCN was heated at 80−90 °C for 96 h. After treatment, 9.70 g of a mixture containing 86% *Z*-**8**, 7% *E*-**8**, 1% *syn*-**7** and 4% unidentified products was

obtained. After distillation, 7.30 g of 4-chloro3-fluoro-pent-2-ene **8** (*Z*/*E* = 12 : 1; yield, 74%; bp 110−111 °C) were obtained.

(*Z*)-4-Chloro-3-fluoropent-2-ene *Z*-8

^{1}H NMR ($CDCl_3$, 200.1 MHz) δ (ppm): 4.95 (dq, 35.1 Hz, 6.9 Hz, 1H, CH=), 4.51 (dq, 18.5 Hz, 6.8 Hz, 1H, CHCl), 1.67—1.61 (m, 6H, $2CH_3$); ^{19}F NMR ($CDCl_3$, 188.3 MHz) δ (ppm): –123.2 (ddq, 35.1 Hz, 18.5 Hz, 2.5 Hz); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ (ppm): 158.0 (d, 252 Hz, CF), 102.8 (d, 16 Hz, CH=), 54.4 (d, 30 Hz, CHCl), 21.9 (d, 3 Hz, CH_3), 8.9 (d, 5 Hz, CH_3); mass spectrum (*m*/*z*, %): 122, 124 (M^+, 24, 7), 107, 109 (M^+–CH_3, 6, 2), 87 (M^+–Cl, 100), 59 (49).

(*E*)-4-Chloro-3-fluoropent-2-ene *E*-8

^{1}H NMR ($CDCl_3$, 200.1 MHz) δ (ppm): 5.17 (dq, 19.5 Hz, 7.5 Hz, 1H), 4.91 (dq, 27.2 Hz, 7.0 Hz, 1H), 1.65—1.59 (m, 6H, $2CH_3$); ^{19}F NMR ($CDCl_3$, 188.3 MHz) δ (ppm): –123.6 (ddq, 27.2 Hz, 19.5 Hz, 2.8 Hz); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ (ppm): 103.3 (d, 16 Hz, CH=), 49.6 (d, 30 Hz, CHCl), 21.4 (d, 3 Hz, CH_3), 10.3 (d, 8 Hz, CH_3); mass spectrum (*m*/*z*, %): 122, 124 (M^+, 34, 12), 107, 109 (M^+–CH_3, 6, 2), 87 (M^+–Cl, 100), 59 (39).

Isomerization of 7-chloro-7-fluorobicyclo[4.1.0]heptane 9

According to method B, a mixture of 5.94 g (40 mmol) of **9**, 398 mg (4.0 mmol) of CuCl, 178 mg (4.2 mmol) of LiCl and 20 ml of MeCN was heated at 80 °C for 24 h. After treatment, 5.90 g of a mixture containing 63% **10**, 2% **11** and 34% *exo*-Cl-**9** were obtained. After distillation, 2.64 g of 3-chloro-2-fluorocycloheptene **10** (yield, 68% on an *endo*-Cl-**9** basis; bp 44−45 °C / 6 Torr).

3-Chloro-2-fluorocycloheptene 10

^{1}H NMR ($CDCl_3$, 200.1 MHz) δ (ppm): 5.54 (dtd, 21.4 Hz, 6.3 Hz, 1.3 Hz, 1H, CH=), 4.69 (m, 1H, CHCl), 2.20—1.40 (m, 8H, $4CH_2$); ^{19}F NMR ($CDCl_3$, 188.3 MHz) δ (ppm): -100.7 (dd, 21.4 Hz, 14.2 Hz); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ (ppm): 159.7 (d, 247 Hz, CF=), 111.4 (d, 21 Hz, CH=), 58.9 (d, 34 Hz, CHCl), 32.7 (d, 8 Hz, CH_2), 26.7 (s, CH_2), 23.3 (s, CH_2), 22.7 (d, 10 Hz, CH_2); mass spectrum (*m*/*z*, %): 148, 150 (M^+, 29, 10), 113 (M^+-Cl, 64), 112 (M^+–Cl–H, 30), 97 (100), 93 (31), 91 (23), 85 (37), 77 (21), 72 (26).

2-Fluorocyclohepta-1,3-diene 11

^{19}F NMR ($CDCl_3$, 188.3 MHz) δ (ppm): -104.4 (m); mass spectrum (*m*/*z*, %): 112 (M^+, 47), 111 (M^+–H, 14), 97 (100), 91 (13), 84 (28), 84 (19).

Isomerization of 1-chloro-1-fluoro-2-vinylcyclopropane 12a

According to method B, a mixture of 9.64 g (80 mmol) of **12a**, 794 mg (8.0 mmol) of CuCl, 345 mg (8.1 mmol) of LiCl and 40 ml of MeCN was heated at 80−90 °C for 20 h. After treatment, 9.16 g of a mixture containing 79% *E*-**14a**, 2% *Z*-**14a**, 15% *Z*-**13a** and 2% *E*-**13a** (yield, 95%; bp 77−79 °C / 155 Torr) were obtained.

(3*Z*)-5-Chloro-4-fluoropenta-1,3-diene *Z*-13a

^{1}H NMR ($CDCl_3$, 300.1 MHz) δ (ppm): 6.59 (ddd, 17.3 Hz, 10.1 Hz, 10.1 Hz, 1H, –CH=), 5.62 (dd, 31.7 Hz, 10.1 Hz, 1H, –CH=CF–), 5.30 (d, 17.3 Hz, 1H, $=CH_2$), 5.19 (d, 10.1 Hz, 1H, $=CH_2$), 4.11 (d, 18.2 Hz, 2H, CH_2Cl); ^{19}F NMR ($CDCl_3$, 282.4 MHz) δ (ppm): –111.6 (dt, 31.7 Hz, 18.2 Hz); mass spectrum (*m*/*z*, %): 120, 122 (M^+, 43, 14), 85 (M^+–Cl, 100), 65 (M^+–Cl–HF, 31).

(3*E*)-5-Chloro-4-fluoropenta-1,3-diene *E*-13a

^{1}H NMR ($CDCl_3$, 300.1 MHz) δ (ppm): 6.33 (ddd, 15.3 Hz, 10.1 Hz, 10.1 Hz, 1H, –CH=), 5.97 (dd, 16.2 Hz, 10.1 Hz, 1H, –CH=CF–), 5.32 (d, 15.3 Hz, 1H, $=CH_2$), 5.23 (d, 10.1 Hz, 1H, $=CH_2$), 4.23 (d, 20.4 Hz, CH_2Cl); ^{19}F NMR ($CDCl_3$, 282.4 MHz) δ (ppm): –107.3 (dt, 20.4 Hz, 16.2 Hz); mass spectrum (*m*/*z*, %): 120, 122 (M^+, 42, 13), 85 (M^+–Cl, 100), 65 (M^+–Cl–HF, 32).

(3*E*)-5-Chloro-2-fluoropenta-1,3-diene *E*-14a

^{1}H NMR ($CDCl_3$, 300.1 MHz) δ (ppm): 6.18—6.10 (m, 2H, –CH=CH–), 4.70 (dd, 15.9 Hz, 4.1 Hz, 1H, $=CH_2$), 4.56 (dd, 48.1 Hz, 4.1 Hz, 1H, $=CH_2$), 4.16 (d, 6.1 Hz, 2H, CH_2Cl); ^{19}F NMR ($CDCl_3$, 282.4 MHz) δ (ppm): –111.0 (ddd, 48.1 Hz, 25.6 Hz, 15.9 Hz); mass spectrum (*m*/*z*, %): 120, 122 (M^+, 41, 11), 85 (M^+–Cl, 100), 65 (M^+–Cl–HF, 34).

(3*Z*)-5-Chloro-2-fluoropenta-1,3-diene *Z*-14a

^{19}F NMR ($CDCl_3$, 282.4 MHz) δ (ppm): –103.7 (ddd, 48.0 Hz, 28.1 Hz, 17.2 Hz); mass spectrum (*m*/*z*, %): 120, 122 (M^+, 40, 10), 85 (M^+–Cl, 100), 65 (M^+–Cl–HF, 36).

Isomerization of 1-chloro-1-fluoro-2-methyl-2-vinylcyclopropane 12b

According to method A, a mixture of 2.00 g (15 mmol) of **12b**, 0.59 g (6 mmol) of CuCl and 10 ml of MeCN was stirred at 80 °C for 10 h. After treatment, 1.81 g of a mixture containing 81% *E*-**14b**, 5% *Z*-**14b**, 7% *Z*-**13b** and 7% *E*-**13b** (yield, 91%) were obtained.

(3*Z*)- or (3*E*)-5-Chloro-4-fluoro-3-methylpenta-1,3-diene *Z*- or *E*-13b

^{1}H NMR ($CDCl_3$, 300.1 MHz) δ (ppm): 6.51 (ddd, 17.0 Hz, 10.0 Hz, 2.0 Hz, 1H, –CH=), 5.38 (br.d, 17.0 Hz, 1H, $=CH_2$), 5.24 (dd, 10.0 Hz, 1.8 Hz, 1H, $=CH_2$), 4.33 (d, 22.9 Hz, 2H, CH_2Cl), 1.84 (d, 3.5 Hz, 3H, CH_3); ^{19}F NMR ($CDCl_3$, 282.4 MHz) δ (ppm): –109.6 (br.t, 22.9 Hz); mass

spectrum (*m*/*z*, %): 99 (M^+–Cl, 31), 79 (M^+–Cl–HF, 81), 53 (31), 51 (61), 45 (32), 39 (50), 27 ($C_2H_3^+$, 100).

(3*E*)- or (3*Z*)-5-Chloro-4-fluoro-3-methylpenta-1,3-diene *E*- or *Z*-13b

^{1}H NMR ($CDCl_3$, 300.1 MHz) δ (ppm): 6.87 (ddd, 17.5 Hz, 10.8 Hz, 1.5 Hz, 1H, –CH=), 5.38 (br.d, 17.5 Hz, 1H, CH_2), 5.23 (d, 10.8 Hz, 1H, =CH_2), 4.28 (d, 23.1 Hz, 2H, CH_2Cl), 1.82 (d, 2.9 Hz, 3H, CH_3); ^{19}F NMR ($CDCl_3$, 282.4 MHz) δ (ppm): –113.1 (br.t, 23.1 Hz); mass spectrum (*m*/*z*, %): 99 (M^+–Cl, 43), 79 (M^+–Cl–HF, 76), 77 (57), 53 (24), 51 (63), 45 (32), 39 (43), 27 ($C_2H_3^+$, 100).

(3*E*)-5-Chloro-2-fluoro-3-methylpenta-1,3-diene *E*-14b

^{1}H NMR ($CDCl_3$, 300.1 MHz) δ (ppm): 6.17 (br.t, 7.8 Hz, 1H, C=CH–), 4.80 (dd, 18.4 Hz, 3.1 Hz, 1H, =CH_2), 4.65 (dd, 48.9 Hz, 3.1 Hz, 1H, =CH_2), 4.20 (d, 7.8 Hz, 2H, CH_2Cl), 1.87 (br.s, 3H, CH_3); ^{19}F NMR ($CDCl_3$, 282.4 MHz) δ (ppm): –109.8 (br. dd, 48.9 Hz, 18.4 Hz); mass spectrum (*m*/*z*, %): 99 (M^+–Cl, 32), 79 (M^+–Cl–HF, 71), 77 (52), 53 (40), 51 (82), 45 (40), 39 (55), 27 ($C_2H_3^+$, 100).

(3*Z*)-5-Chloro-2-fluoro-3-methylpenta-1,3-diene *Z*-14b

^{19}F NMR ($CDCl_3$, 282.4 MHz) δ (ppm): –100.2 (br. dd, 48.7 Hz, 19.1 Hz); mass spectrum (*m*/*z*, %): 99 (M^+–Cl, 31), 79 (M^+–Cl–HF, 72), 77 (50), 53 (42), 51 (82), 45 (42), 39 (55), 27 ($C_2H_3^+$, 100).

Isomerization of 2-chloro-2-fluoro-1,1`-bi(cyclopropyl) 15

According to method A, a mixture of 271 mg (2.0 mmol) of **15**, 197 mg (2.0 mmol) of CuCl and 2 ml of MeCN was stirred at 80 °C for 6 h. Reaction was monitored by GLC analysis. After the treatment of the reaction mixture, 163 mg of **16** (yield, 60%) were obtained.

(3*E*)-6-Chloro-2-fluorohexa-1,3-diene 16

^{1}H NMR ($CDCl_3$, 200.1 MHz) δ (ppm): 6.15—5.85 (m, 2H, CH=CH), 4.65 (dd, 16.5 Hz, 2.8 Hz, 1H, =CH_2), 4.41 (dd, 48.6 Hz, 2.8 Hz, 1H, =CH_2), 3.58 (t, 6.8 Hz, 2H, CH_2Cl), 2.59 (m, 2H, CH_2); ^{19}F NMR ($CDCl_3$, 188.3 MHz) δ (ppm): -111.6 (ddd, 48.6 Hz, 25.7 Hz, 16.5 Hz); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ (ppm): 161.5 (d, 252 Hz, CF=), 128.6 (d, 4 Hz, CH=), 124.4 (d, 25 Hz, CH=), 92.9 (d, 21, =CH_2), 43.4 (s, CH_2Cl), 35.4 (s, CH_2).

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