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Synthesis of hydrofluorocycloolefins through dehydrofluorination of hydrofluorocycloalkanes in amide solvents

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ABSTRACT

Hydrofluorocycloolefins have outstanding economic and environmental advantages, as well as huge application potentials owing to their zero ozone depletion potentials (ODP) values and low global warming potentials (GWP) values. The synthesis of hydrofluorocycloolefins through dehydrofluorination of hydrohalocycloalkanes in *N,N*-dimethylformamide (DMF) or *N,N*-dimethylacetamide (DMAC) was investigated. It was found that the presence of −CHF− is critical for efficient elimination of HF. The reaction using reagents containing −CHF− group proceeded very well, whereas elimination was much more difficult to occur for reactants without −CHF− group. Based on these results, a rational reaction mechanism was proposed.

1. Introduction

The promulgation of the Montreal and Kyoto protocols brought forward the global issue of ozone depletion caused by chlorofluorocanbons (CFCs) and hydrochlorofluorocarbons (HCFCs) [1]. To address the issue, novel substances for zero ozone depletion potentials (ODP) values and low global warming potentials (GWP) values are extensively explored. Hydrofluorocarbons (HFCs) are one of the developed ozone depletion substitutes (ODS), among which hydrofluoroolefins have attracted tremendous attention by virtue of their zero ODP values and short atmospheric lifetimes [2–4]. Herein, particular interest was paid to hydrofluorocycloolefins owing to their outstanding economic and environmental advantages, as well as huge application potentials. As basic raw materials, hydrofluorocycloolefins are also widely used for the production of fluorine-containing fine chemicals and polymer materials such as rocket propellant composites [5], refrigerants [6,7], blowing agents [8,9], etchants [10], cleaning agents [11], fire extinguishing agents [12], sprays [13], and heat pumping fluids [14,15].

Generally, hydrofluorocycloolefins can be prepared through several different ways as follows, which were summarized in Scheme 1. (1) Liquid-phase H−X (X = F, Cl) exchange, a reaction occurs between fluorocycloolefins and sodium borohydride, which provides hydrogen [16–18], under an ultra-low temperature condition in mixing solvents of lithium tetrahydrogen aluminum (LAH) and ether; (2) Catalytic gas-phase H−Cl exchange, which occurs between hydrofluorocycloolefins and hydrogen gas (H_2) in quartz reactor [19] catalysed by chromium-nickel or in fixed bed reactor [20] in the presence of catalyst whose active component was palladium; (3) Catalytic isomerisation of hydrofluorocycloolefins [21]; (4) HX (X = F, Cl, Br) elimination from hydrohalofluorocycloalkanes in strong base [9,22–25]. In reality, the harsh reaction condition in method (1) prevents its popularity. Meanwhile, methods (2) and (3) always suffer low selectivity for hydrofluorocycloolefins, generating a mass of by-products that are difficult to separate. For example, the gas-phase H−X exchange between 1,2-dichlorotetrafluorocyclobutene and H_2 with chromium-nickel catalyst at 250 °C produces a mixture of 1,2-dihydrotetrafluorocyclobutene (HFO-c1334zz, selectivity of 44%, boiling point of 54 °C), 1,1,2,2-tetrafluorocyclobutane (HFC-c354cc, selectivity of 24%, boiling point of 50 °C), and 1-chloro-3,3,4,4-tetrafluorocyclobutene (HCFO-c1324xz, selectivity of 25%, boiling point of 59 °C) that are difficult to separate due to their azeotropic feature [19]. As a result, method (4), namely, dehydrofluorination of hydrofluorocycloalkanes, remains a primary approach for the synthesis of hydrofluorocycloolefins.

In this study, we reported a facile method for the synthesis of hydrofluorocycloolefins through dehydrofluorination of hydrofluorocycloalkanes in *N,N*-dimethylformamide (DMF) or *N,N*-dimethyl acetamide (DMAC) under mild conditions. So far, it has rarely been reported that amide solvent is able to serve as a dehydrofluorinated reagent. DMF and DMAC are employed because their unique acid-base properties [26] enabled successful elimination of HF as reported by our team [27]. To verify the applicability of this novel synthetic strategy, a number of hydrofluorocycloalkanes, including 1,1,2,2,3,3,4-heptafluorocyclopentane (HFC-c447ef), cis-1,1,2,2,3,3,4,4-octafluorocyclopentane (HFC-c438ee (cis)),

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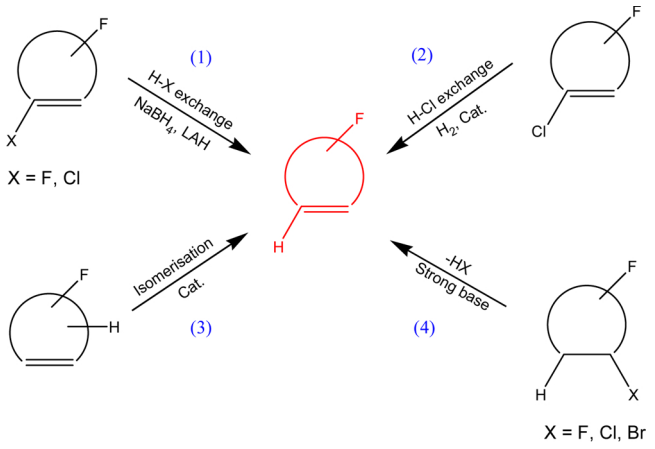


Scheme 1. Existing routes to synthesize hydrofluorocycloolefins.

1,1,2,2,3-pentafluorocyclobutane (HFC-c345ef), cis-1,1,2,2,3,4-hexafluorocyclobutane (HFC-c336ee (cis)), 1,1,2,2,3,3-hexafluorocyclopentane (HFC-c456ff), and 1-chloro-1,3,3-trifluorocyclobutane (HCFC-c353cfb), were carefully investigated. The results illustrated that dehydrofluorination occurred very well in reactants containing −CHF− group. Elimination of HF was much more difficult to take place in reactants without −CHF− group. We therefore concluded that the presence of −CHF− group was indispensable for efficient dehydrofluorination of hydrofluorocycloalkanes, and a reaction mechanism was proposed.

2. Results and discussion

2.1. Dehydrofluorination of hydrofluorocycloalkanes

The details of dehydrofluorination for all the hydrofluorocycloolefins, including reaction route, conversion rate, and selectivity for each corresponding product, were summarized in Scheme 2. The conversion rate of HFC-c447ef (83.3% in DMF and 83.2% in DMAC) (Eq 1) is higher than that of HFC-c438ee (cis) (42.1% in DMF and 45.7% in DMAC) (Eq 2). Similarly, the conversion rate of HFC-c345ef (36.8% in DMF and 11.9% in DMAC) (Eq 3) is higher than that of HFC-c336ee (cis) (8.5% in DMF and 1.3% in DMAC) (Eq 4). No dehydrofluorination occurred for HFC-c456ff and HCFC-c353cfb in both DMF and in DMAC as illustrated (Eq 5) and (Eq 6), respectively.

According to the comparison of the reaction outcomes between (Eq 1) and (Eq 2), as well as those between (Eq 3) and (Eq 4), the dehydrofluorination from −CHF−CH_2− located at −$(CF_2)_n$−CHF−CH_2− (n = 2, 3) occurred more easily than the that from −CHF−CHF− located at −$(CF_2)_n$−CHF−CHF− (n = 2, 3), which can be rationalized by stronger elimination reactivity of −CHF−CH_2− located at −$(CF_2)_n$−CHF−CH_2− (n = 2, 3) than that of −CHF−CHF− located at −$(CF_2)_n$−CHF−CHF− (n = 2, 3) [28,29]. In (Eq 2), a small amount of HFO-c1427yyce was formed due to the isomerization of HFO-c1427yye in the presence of fluorine anion [30].

Comparison of the selectivity for each product in (Eq 2) and (Eq 4) implies that the loss of a fluorine from −CHF− group was easier than the loss of a fluorine from −CF_2− group in −$(CF_2)_n$−CHF−CHF− (n = 2, 3) [28,31,32]. Besides, the selectivity of each products in (Eq 1) and (Eq 3) suggested easier removal of a hydrogen from −CH_2− group than that from −CHF− group in −$(CF_2)_n$−CHF−CH_2− (n = 2, 3) [33–35]. Furthermore, the higher conversion rates of (Eq 1) (or (Eq 2)) than that of (Eq 3) (or (Eq 4)) confirmed a lower reactivity of four-membered hydrofluorocycloalkane than that of five-membered hydrofluorocycloalkane. This is probably because the carbanion intermediates are less stable in four-membered ring than in five-membered ring [17,36].

As to dehydrofluorination of HFC-c345ef in (Eq 3) and that of HFC-c336ee (cis) in (Eq 4), there both were higher conversion rate in DMF than in DMAC. Such a trend might be caused by a lower alkalinity of DMAC than DMF [26], because DMF could be decomposed into a strong alkaline dimethylamine after heating. As a result, the elimination reaction occurred more easily in DMF than in DMAC. However, both HFC-c447ef and HFC-c438ee (cis) exhibited similar conversion rates in DMF and DMAC, which could be attributed to easier removal of the β-hydrogen of fluorine in five-membered hydrofluorocycloalkane than that in four-membered one [17,25,36]. Therefore, the basicity of solvent was not a decided factor for dehydrohalogenation in five-membered hydrofluorocycloalkane.

The failure of dehydrohalogenation for HFC-c456ff and HCFC-c353cfb illustrated that dehydrohalogenation would not occur for reactants containing only −CH_2−, −CFCl− or −CF_2− but no −CHF− group. This was probably because the extremely weak acidity of hydrogen induced by fluorine from −CH_2−CH_2−CFX− group prevented itself from leaving and the strong strength of C−Cl bond in −CFCl− group and C−F bond in −CF_2− group prevented the removal of halogen from −CFCl− and −CF_2− groups [28,29,33–35].

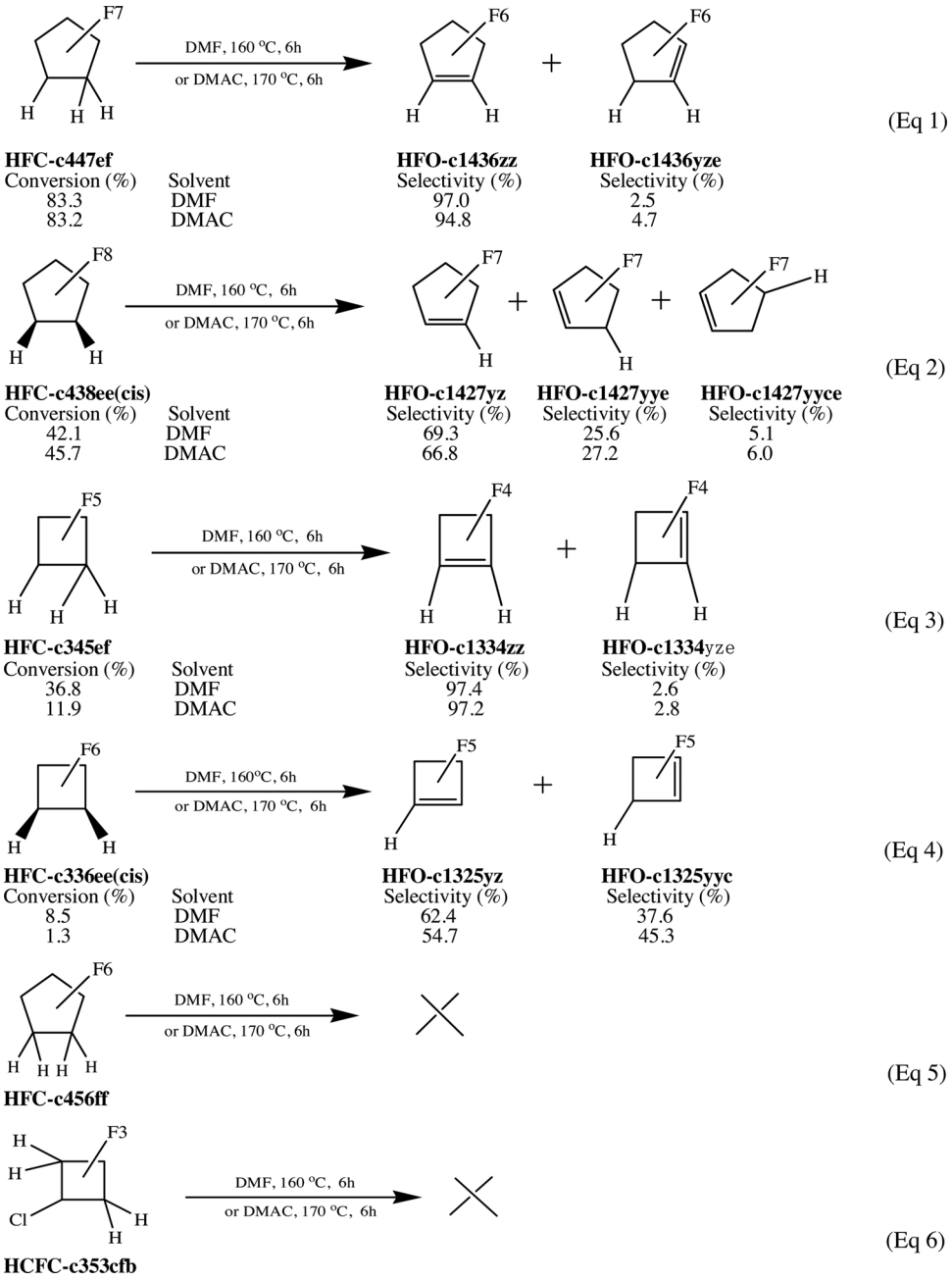
2.2. Mechanism of dehydrofluorination

In view of the above experimental results, the mechanism of dehydrofluorination of hydrofluorocycloalkanes containing −CFR^1−CHR^2− (R^1 = F, H; R^2 = F, H) group in DMF or DMAC was proposed in Scheme 3.

It should be noted that DMAC ($CH_3CON(CH_3)_2$) is thermally stable but DMF ($HCON(CH_3)_2$) easily decomposes into dimethylamine ($HN(CH_3)_2$) and carbon monoxide (CO) under heating [37,38]. Therefore, under the current reaction condition (160 °C in DMF and 170 °C in DMAC) (Scheme 2), the actual species coming into play are dimethylamine and DMAC (see Scheme 3, R^3 = H and CH_3CO in $R^3N(CH_3)_2$). Initially, the lone pair electrons on the nitrogen of $R^3N(CH_3)_2$ [26] attacked and removed the acidic β-hydrogen of fluorine (the hydrogen atom located on the carbon adjacent to the carbon substituted with fluorine) in hydrofluorocycloalkane [34,35,39] by forming a protonated intermediate, namely, $R^3(HN^+)(CH_3)_2$ [39]. The elimination of hydrogen led to the formation of a carbanion whose electron pair was stabilized by the strong induction effect of fluorine [31,32,39,41–44]. This fluorine was then removed as fluoride anion (F^-), generating hydrofluorocycloolefin as the final product. Notably, the F- was stabilized by forming electrically neutral $[R^3(HN^+)(CH_3)_2]F^-$ with the protonated intermediate $(R^3(HN^+)(CH_3)_2)$ [40,45]. In other words, the protonated intermediate made fluorine a much better leaving group. In short, the hydrogen fluoride was eliminated from the hydrofluorocycloalkane via E1cB elimination.

The −CF_2−CHF−CH_2−CF_2− (in **HFC-c447ef** and **HFC-c345ef**) and −CHF−CHF−CF_2− (in **HFC-c438ee (cis)** and **HFC-c336ee (cis)**) are both highly fluorinated groups. In these groups, the relative acidity of β-hydrogen ranked in an order of −CH_2− > −CHF− [33–35]. Therefore, the loss of hydrogen from −CH_2− was more preferred than that from −CHF− group. On the other hand, due to the strong strength of C−F bond, the leaving ability of fluorine followed an order of −CHF− > −CF_2− [33–35], which resulted in easier removal of fluorine from −CHF− than from −CF_2− group.

According to the above rules, the ease of dehydrohalogenation of the −CF_2−CHF−CH_2−CF_2− group followed an order of −CF_2−CH=CH−CF_2− > −CF_2−CHF−CH = CF− > > −CF=CF−CH_2−CF_2−, which agreed well with the higher selectivity for HFO-c1436zz (97.0% in DMF and 94.8% in DMAC) than HFO-c1436yze (2.5% in DMF and 4.7% in DMAC) in the dehydrohalogenation of **HFC-c447ef** (Eq 1), as well as the higher selectivity for HFO-c1334zz (97.4% in DMF and 97.8% in DMAC) and HFO-c1334yze (2.6% in DMF and 2.8% in DMAC) in the dehydrohalogenation of **HFC-c345ef** (Eq 3). Similarly, the ease of dehydrohalogenation of −CHF−CHF−CF_2− group is in an order of −CF = CH−CF_2− > −CHF−CF = CF−, which was also in accordance with the higher selectivity for HFO-c1427yz (69.3% in DMF and 66.8% in DMAC) than HFO-c1427yye (25.6% in DMF and 27.2% in DMAC) in



Scheme 2. Novel methods for preparation of hydrofluorocycloolefins.

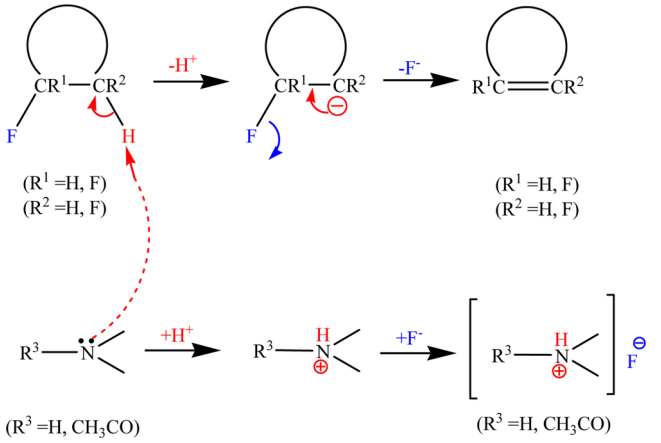
the dehydrohalogenation of **HFC-c438ee (cis)** (Eq 2) as well as the higher selectivity for HFO-c1325yz (62.4% in DMF and 54.7% in DMAC) than HFO-c1325yyc (37.6% in DMF and 45.3% in DMAC) in the dehydrohalogenation of **HFC-c336ee (cis)** (Eq 4).

For cyclic halides, conformational effect should not be neglected because it dominates the ratio of elimination products with different conformations [32], for instance, trans- and cis- conformations. Although trans-elimination was generally easier, generation of comparable cis- and trans- products from the elimination of cyclic halides is also frequently reported [16,41,46,47]. We therefore examined the conformation effect for the elimination of our molecular system. It was found that main products from the elimination of **HFC-c438ee (cis)** and **HFC-c336ee (cis)**, namely, HFO-c1427yz (Eq 2) and HFO-c1325yz (Eq 4), were both derived from trans-elimination of fluorine and hydrogen that are of antiperiplanar conformation. However, it seems that all the products from (Eq 1) to (Eq 4) originated from both cis- and trans- elimination of the fluorine and hydrogen atoms that of both coplanar and antiperiplanar positions.

In the case of $-CH_2-CH_2-CF_2-$ (in **HFC-c456ff**) and $-CF_2-CH_2-CFCl-$ (in **HCFC-c353cfb**) groups, among which the hydrogen had such extremely weak acidity owing to the strong induction effect of fluorine that it was quite difficult to leave. In addition, the strong C—F and C—Cl bonds prevented the leaving of fluorine and chlorine [28,48,49]. Therefore, no elimination of hydrogen halide occurred, as displayed in (Eq 5) and (Eq 6).

3. Conclusions

The dehydrohalogenation of hydrohalocycloalkanes in DMF or DMAC was systematically investigated by using a series of four-membered and five-membered hydrofluorocycloalkanes with different extents of fluorination. It was found that the dehydrofluorination



Scheme 3. The mechanism of dehydrofluorination of hydrofluorocycloalkanes.

proceeded very well in reactants containing —CHF— group. Elimination was much more difficult to occur in reactants without —CHF— group. We thus notified the importance of the presence of —CHF— group for smooth dehydrofluorination of hydrohalocycloalkanes. Base on the experimental results, a rational reaction mechanism was proposed. Our study not only demonstrates a facile approach for synthesizing hydrofluocycloolefins with high selectivity under relatively mild condition, but also provides in-depth understanding of the reaction mechanism which will guide efficient production of various hydrofluocycloolefins in future.

4. Experimental section

4.1. Chemicals

The reagents 1,1,2,2,3,3,4-heptafluorocyclopentane (**HFC-c447ef**, 99.0 + %), cis-1,1,2,2,3,3,4,5-octafluorocyclopentane (**HFC-c438ee (cis)**, 99.0 + %) and 1,1,2,2,3,3-hexafluorocyclopentane (**HFC-c456ff**, 99.0 + %) were purchased from Shaanxi Shenguang Chemical Industry Chemical Co., Ltd. The reagents 1,1,2,2,3-pentafluorocyclobutane (**HFC-c345ef**, 99.0 + %), cis-1,1,2,2,3,4-hexafluorocyclobutane (**HFC-c336ee (cis)**, 99.0 + %), 1,1,3-pentafluoro-3-chloro-cyclobutane (**HCFC-c353cfb**, 99.0 + %), *N,N*-dimethylformamide (DMF) and *N,N*-dimethylacetamide (DMAC) were purchased from Wako Pure Chemical Industries, Ltd. Chloroform-d ($CDCl_3$, 99.8 atom%D) at was obtained from Aldrich Chem. Co. (Japan). $CFCl_3$ (CFC-11, 99.0 + %) was purchased from Synquest Labs, Lnc.

4.2. Instrument

The 2000 mL stainless steel reactor was used for all experiments with magnetic stirring using a Magmix stirrer tough mixer (MRK Co., LTD.).

The ^1H, ^{13}C and ^{19}F NMR spectra of HFC-c447ef, HFC-c438ee (cis) and HFC-c456ff were cited from the literature [50]. The ^1H, ^{13}C and ^{19}F NMR spectra of HFO-c1436zz, HFO-c1436yze, HFO-c1427yz, HFO-c1427yye, HFO-c1427yyce and HFO-c1427yyce were cited from the literature [30]. The ^{19}F NMR spectra of HFC-c345ef, HFO-c1334zz, HFC-c336ee (cis), HFO-c1325yz, HFO-c1325yyc and HCFC-c353cfb were recorded on a Bruker AVANCE 400 (400 MHZ) at 25 °C with $CFCl_3$ as internal references in $CDCl_3$ solvent. The ^{13}C and ^1H NMR spectra of HFC-c345ef, HFO-c1334zz, HFC-c336ee (cis), HFO-c1325yz, HFO-c1325yyc and HCFC-c353cfb were recorded on a Bruker AVANCE 400 (400 MHZ) at 25 °C in $CDCl_3$. The patterns were compared with those of authentic samples.

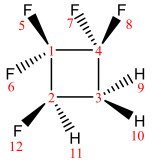
The gas chromatograph was a Shimadzu GC-2014S with DB-WAX column with 30 m length and 0.25 mm inner diameter (film: 0.25 μm) from Agilent Technologies Inc. The operating conditions of the GC were as follows: 40 °C for 10 min; 10 °C/min to 240 °C; hold for 10 min. Both the injection port and the thermal conductively were maintained at 240 °C, and the carrier gas was a mixture of H_2, He and air introduced at a rate of 3 mL/min.

4.3. Experiment procedure

The dehydrofluorination reactions of all reactants including HFC-c447ef, HFC-c345ef, HFC-c438ee (cis), HFC-c336ee (cis), HFC-c456ff and HCFC-c353cfb were identically designed and conducted according to following conditions. The molar ratio of DMF or DMAC and each reactant was 2/1. The mixture of DMF or DMAC and each reactant were placed into a 2000 mL stainless steel reactor equipped with an electric heater and an agitating device. The reactor was heated to a temperature of 160 °C in DMF solvent and being stirred for 6 h under magnetic stirring, while the reactor was heated to a temperature of 170 °C in DMAC solvent and being stirred for 6 h under magnetic stirring. The products from the above system were detected by GC and NMR, respectively.

4.4. Analytic results

4.4.1. HFC-c345ef



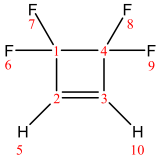
MS data (*m/z*): 146 (M^+), 127 (M^+–F), 113 (M^+–CH_2F), 107 (M^+–HF_2), 100 (M^+–C_2H_3F), 95 (M^+–CHF_2), 93 (M^+–CH_3F_2), 82 (M^+–$C_2H_2F_2$), 77 (M^+–CF_3), 75 (M^+–CH_2F_3), 69 (M^+–HF_4), 63 (M^+–$C_2H_2F_3$), 57 (M^+–CHF_4), 45 (M^+–C_2HF_4), 37 (M^+–CH_2F_5).

^{19}F NMR (377 MHz, $CDCl_3$): δ −202.77 (s, F5, 1 F), −135.21 (d, J = 220.2 Hz, F6, 1 F), −118.81 (d, J = 219.8 Hz, F8, 1 F), −116.01 (d, J = 217.5 Hz, F7, 1 F), −113.95 (d, J = 204.0 Hz, F12, 1 F).

^1H NMR (400 MHz, $CDCl_3$): δ 2.69 (m, H9 and H10, 2 H), 5.16 (d, J = 52.4 Hz, H11, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 37.32 (qd, J = 22.67 Hz, C3, 1C), 84.05 (dm, J = 224.12 Hz, C2, 1C), 115.60 (tm, J = 277.14 Hz,C4, 1C), 115.61 (tq, J = 290.88 Hz,C1, 1C).

4.4.2. HFO-c1334zz



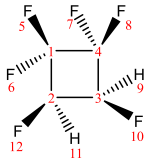
MS data (*m/z*): 126 (M^+), 107 (M^+–F), 100 (M^+–C_2H_2), 88 (M^+–F_2), 87 (M^+–HF_2), 75 (M^+ − CHF_2), 69 (M^+–F_3), 63 (M^+–C_2HF_2), 50 (M^+–$C_3H_2F_2$), 44 (M^+–C_2HF_3), 38 (M^+–CF_4), 37 (M^+–CHF_4).

^{19}F NMR (377 MHz, $CDCl_3$): δ −111.02 (d, J = 3.77 Hz, F6, F7, F8 and F9, 4 F).

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.82 (m, H5 and H10, 2 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 119.28 (tm, J = 286.64 Hz, C1 and C4, 2C), 142.56 (quint, J = 19.19 Hz, C2 and C3, 2C).

4.4.3. HFC-c336ee (cis)



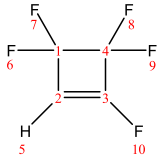
MS data (*m/z*): 164 (M^+), 145 (M^+–F), 113 (M^+–CHF_2), 100 (M^+–$C_2H_2F_2$), 95 (M^+–CF_3), 82 (M^+–C_2HF_3), 75 (M^+–CHF_4), 64 (M^+–C_2F_4), 57 (M^+–CF_5), 44 (M^+–C_2HF_5), 37 (M^+–CHF_6).

^{19}F NMR (377 MHz, $CDCl_3$): δ –224.03 (d, J = 50.90 Hz, F10 and F12, 2 F), −134.11 (d, J = 233.36 Hz, F6 and F7, 2 F), −119.56 (d, J = 233.36 Hz, F5 and F8, 2 F).

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.12 (dm, J = 52 Hz, H9 and H11, 2 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 83.99 (dm, J = 232.81 Hz, C2 and C3, 2C), 113.92 (tm, J = 297.24 Hz, C1 and C4, 2C).

4.4.4. HFO-c1325yz



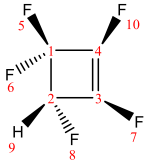
MS data (*m/z*): 144 (M^+), 125 (M^+–F), 113 (M^+–CF), 106 (M^+–F_2), 100 (M^+–C_2HF), 93 (M^+–CHF_2), 81 (M^+–C_2HF_2), 74 (M^+–CHF_3), 63 (M^+–C_2F_3), 56 (M^+–CF_4), 44 (M^+–C_2F_4), 37 (M^+–CF_5).

^{19}F NMR (377 MHz, $CDCl_3$): δ −118.20 (m, F8 and F9, 2 F), −113.48 (m, F6 and F7, 2 F), −104.04 (m, F10, 1 F).

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.96 (dd, J = 26.0, 6.8 Hz, H5, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 115.52 (tm, J = 280.28 Hz, C4, 1C), 117.15 (tm, J = 277.04 Hz, C1, 1C), 156.07 (quint, J = 25.0 Hz, C3, 1C), 159.51 (quint, J = 25.0 Hz, C2, 1C).

4.4.5. HFO-c1325yyc

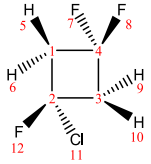


MS data (*m/z*): 144 (M^+), 125 (M^+–F), 113 (M^+–CF), 106 (M^+–F_2), 93 (M^+–CHF_2), 81 (M^+–C_2HF_2), 74 (M^+–CHF_3), 63 (M^+–C_2F_3), 56 (M^+–CF_4), 44 (M^+–C_2F_4), 37 (M^+–CF_5).

^{19}F NMR (377 MHz, $CDCl_3$): δ −187.1 (m, F8, 1 F), −127.4 (dtt, J = 17.6, 10.7, 1.9 Hz, F10, 1 F), −122.5 (m, F7, 1 F), −119.6(dq, J = 198.4, 17.1, 15.5, 10.4 Hz, F6, 1 F), −113.1 (m,F5, 1 F).

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.44 (dq, J = 63.4, 17.2, 4.6, 1.2 Hz, H9, 1 H).

4.4.6. HCFC-c353cfb



MS data (*m/z*): 144 (M^+), 125 (M^+–F), 109 (M^+–CH_4F), 105 (M^+–HF_2), 95 (M^+–CH_2Cl), 89 (M^+–HFCl), 80 (M^+–$C_2H_2F_2$), 75 (M^+–CH_3FCl), 64 (M^+–C_2H_2FCl), 59 (M^+–CF_2Cl), 57 (M^+–CH_2F_2Cl), 51 (M^+–HF_3Cl), 44 (M^+–$C_2H_3F_2Cl$), 38 (M^+–CH_2F_3Cl).

^{19}F NMR (377 MHz, $CDCl_3$): δ −99.64 (dm, J = 200.19 Hz, F12, 1 F), –114.28 (m, F7, 1 F), −114.79 (m, F8, 1 F).

^{1}H NMR (400 MHz, $CDCl_3$):δ 2.546 (m, H5 and H6, 2 H), 2.602 (m, H9 and H10, 2 H).

^{13}C NMR (101 MHz, $CDCl_3$):δ 28.02 (td, J = 22.12 Hz, C1 and C3, 2C), 106.97 (ddd, J = 294.01 Hz, C2, 1C), 117.00 (ddd, J = 288.25 Hz, C4, 1C).

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