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^{13}C NMR studies of hydrochlorofluoropropanes and chlorofluoropropanes

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Abstract

^{13}C NMR chemical shifts of 3,3-dichloro-1,1,1-trifluoropropanes (CF_3-CXY-$CHCl_2$), 3-chloro-2,2,3,3-tetrafluoropropanes ($CClF_2$-CF_2-R), and diastereomers of 1,3-dichloro-1,1,2,3-tetrafluoropropane were studied by analysis using MNDO calculations. In CF_3-CXY-$CHCl_2$, ^{13}C NMR chemical shifts of the methylene group are dependent on the electronegativity of the atoms attached to the methylene carbon, and those of the trifluoromethyl group depend on the magnetic anisotropy of neighboring halogen atoms X and Y. In $CClF_2$-CF_2-R, the magnetic anisotropy of the atoms gauche to the terminal group and the steric effect of the terminal group are responsible for the ^{13}C NMR chemical shift of a terminal halogenated methyl group, and the inductive effect of the substituent R mainly determines the ^{13}C NMR chemical shift of the difluoromethylene group.

Keywords: Hydrochlorofluoropropanes; Chlorofluoropropanes; ^{13}C NMR chemical shift

1. Introduction

Over the past years we have been studying the correlation between ^{19}F NMR chemical shifts and the molecular structure of halogenated propanes by analysis using MNDO calculations [1–3]. Despite some studies on ^{13}C NMR chemical shifts of mono-halogenated compounds [4,5], there has not been a systematic study of ^{13}C NMR chemical shifts of hydrochlorofluoropropanes and chlorofluoropropanes.

We are concerned with ^{13}C NMR chemical shifts in CF_3-CXY-$CHCl_2$ (X, Y = H, Cl, F), $CClF_2$-CF_2-R, where R is a substituted methyl group containing combinations of H, Cl, F. We also compare ^{13}C NMR chemical shifts with ^{19}F NMR chemical shifts in these compounds.

2. Results and discussion

2.1. *3,3-Dichloro-1,1,1-trifluoropropanes (CF_3-CXY-$CHCl_2$)*

Table 1 lists the ^{13}C and ^{19}F NMR chemical shifts of methylene groups and ^{13}C NMR chemical shifts of trifluoromethyl groups in 3,3-dichloro-1,1,1-trifluoropropanes.

If additivity of the atoms in CXY is assumed, the ^{13}C NMR chemical shifts of the substituted methylene groups and trifluoromethyl groups in 3,3-dichloro-1,1,1-trifluoropropanes (CF_3-CXY-$CHCl_2$) are expressed by the number of H, F and Cl atoms (n(H), n(F) and n(Cl)) in CXY as shown in Eqs. (1) and (2). For CXY

Table 1
^{13}C and ^{19}F chemical shift of CF_3 and CXY groups in CF_3-CXY-$CHCl_2$

-CXY-	CF_3 δ_C (ppm)	CH_3 δ_F (ppm)	CXY δ_C (ppm)
CF_2	118.6	−80.1	110.9
CClF	119.9	−77.1	105.5
CHF	120.9	−75.0	89.5
CCl_2	121.3	−73.1	87.2
CHCl	122.0	−70.9	63.1
CH_2	123.7	−64.8	47.3

$$\delta_C(CXY) = -25.72n(\mathrm{H}) - 6.56n(\mathrm{Cl}) + 6.89n(\mathrm{F}) + 101.93 \qquad (1)$$

and for trifluoromethyl groups

$$\delta_C(CF_3) = 61.74n(\mathrm{H}) + 60.58n(\mathrm{Cl}) + 59.28n(\mathrm{F}) \qquad (2)$$

The relationships between the observed and calculated ^{13}C chemical shifts are listed in Table 2.

Eq. (1) shows that more electronegative atoms tend to lead to larger shifts for the substituted methylene group. ^{13}C NMR chemical shifts of the methylene group are, therefore, dependent on the electronegativity of the atoms attached to the methylene carbon.

In contrast with the case of the methylene group, the regression coefficients for the trifluoromethyl group are in reverse

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Table 2
Observed and calculated ^{13}C chemical shifts of CF_3 and CXY groups in CF_3-CXY-$CHCl_2$

R	CF_3		CXY	
	obs.	calc.	obs.	calc.
CF_2	118.6	118.6	110.9	115.7
CClF	119.9	119.9	105.5	102.3
CHF	120.9	121.0	89.5	83.1
CCl_2	121.3	121.2	87.2	88.8
CHCl	122.0	122.3	63.1	69.6
CH2	123.7	123.5	47.3	50.5
r	0.995		0.980	

order. Let us now compare the ^{13}C chemical shift with the ^{19}F chemical shift of the trifluoromethyl group in 3,3-dichloro-1,1,1-trifluoropropanes (CF_3-CXY-$CHCl_2$). A plot of the ^{13}C chemical shifts vs. the ^{19}F chemical shift of the trifluoromethyl group gives an approximately linear relationship (Fig. 1).

As we elucidated in the previous paper [2], the β-carbon may cause an increase in the paramagnetic terms, and ^{13}C chemical shifts of the trifluoromethyl group in CF_3-CXY-$CHCl_2$ depend on the magnetic anisotropy of neighboring halogen atoms X and Y.

2.2. 3-Chloro-2,2,3,3-tetrafluoropropanes ($CClF_2$-CF_2-R)

Table 3 lists the ^{19}F and ^{13}C chemical shifts of the chlorodifluoromethyl group in 3-chloro-2,2,3,3-tetrafluoropropanes ($CClF_2$-CF_2-R), and a plot of the ^{19}F and ^{13}C chemical shifts are shown in Fig. 2.

As we reported [2], the ^{19}F chemical shift of the chlorodifluoromethyl group in $CClF_2$-CF_2-R is determined by the steric effect, or the bulkiness of the substituent R, but it seems that the magnetic anisotropy as well as the steric effect plays an important role in the ^{13}C chemical shifts.

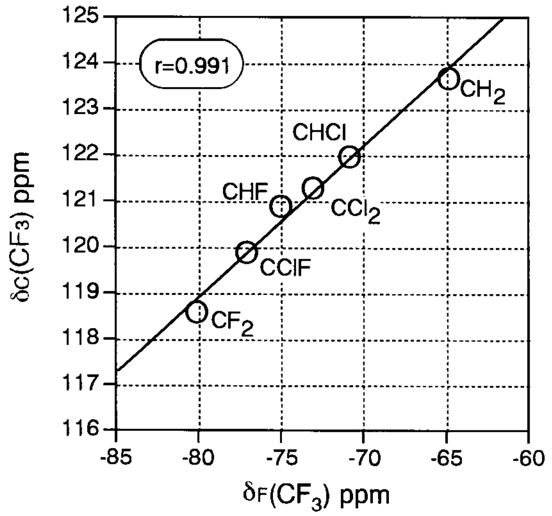

Fig. 1. Correlation between ^{13}C and ^{19}F chemical shifts of CF_3 in CF_3-CXY-$CHCl_2$.

Table 3
^{19}F and ^{13}C chemical shifts of $CClF_2$ in $CClF_2$-CF_2-R

R	$CClF_2$ δ_F (ppm)	$CClF_2$ δ_C (ppm)
CCl_3	−61.3	123.3
CCl_2F	−64.6	122.8
$CHCl_2$	−66.3	122.9
$CClF_2$	−67.7	122.1
CHClF	−69.1	122.7
CF_3	−70.0	121.6
CHF_2	−70.3	122.1
CH_2Cl	−70.4	123.2
CH_2F	−71.0	122.9
CH_3	−72.5	124.0

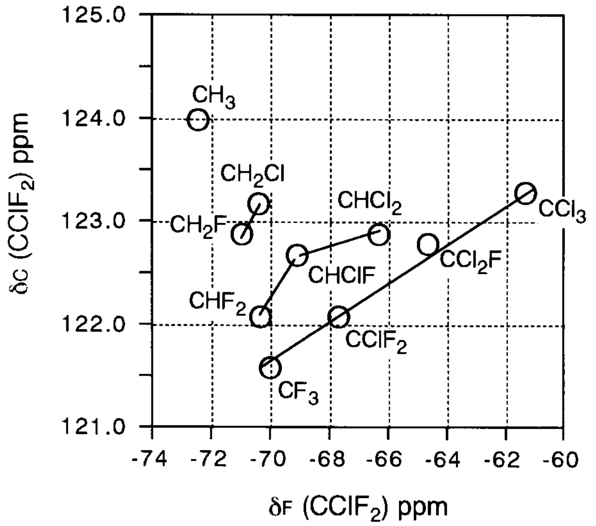

Fig. 2. Correlation between ^{19}F and ^{13}C chemical shifts of $CClF_2$ in $CClF_2CF_2$-R.

We have examined conformations using MNDO calculations to investigate the cause of the ^{13}C chemical shift of the chlorodifluoromethyl group in $CClF_2$-CF_2-R. The heats of formation of all rotamers of $CClF_2$-CF_2-R were calculated as described previously in order to estimate the rotamer population [2]. As X and Y atoms in Fig. 3 are gauche to the carbon atom of the chlorodifluoromethyl group, the average number of gauche pairs of atoms in each rotamer of $CClF_2$-CF_2-CXYZ, i.e. X–Y = H–H, H–Cl, H–F, F–F, F–Cl and Cl–Cl, was calculated. The average carbon frame angles (C–C–C angles) of $CClF_2$-CF_2-CXYZ, as an indication of the steric interaction between $CClF_2$ and CXYZ, were also calculated as listed in Table 4.

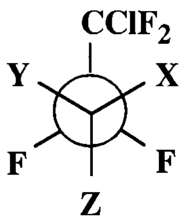

Fig. 3. $CClF_2CF_2$-CXYZ.

Table 4
The average number of atoms in X, Y positions of $CClF_2CF_2$-CXYZ as depicted in Fig. 3 and calculated average C–C–C angles of $CClF_2CF_2$-CXYZ

CXYZ	Average number of atoms in X, Y positions						C–C–C angle (deg)
	n(H–H)	n(H–Cl)	n(H–F)	n(F–F)	n(Cl–F)	n(Cl–Cl)	
CCl_3	0	0	0	0	0	1	117.21
CCl_2F	0	0	0	0	0.892	0.110	115.87
$CClF_2$	0	0	0	0.513	0.488	0	115.00
CF_3	0	0	0	1	0	0	114.41
CH_3	1	0	0	0	0	0	112.96
CH_2Cl	0.804	0.197	0	0	0	0	112.35
CH_2F	0.481	0	0.518	0	0	0	112.40
$CHCl_2$	0	0.969	0	0	0	0.031	114.03
CHF_2	0	0	0.957	0.013	0	0	113.58
CHClF	0	0.044	0.915	0	0.040	0	113.20

Table 5
Observed and calculated ^{13}C chemical shifts of $CClF_2$ in $CClF_2CF_2$-R

R	δ_C ($CClF_2$)	
	obs.	calc.
CCl_3	123.3	123.3
CCl_2F	122.8	122.8
$CClF_2$	122.1	122.2
CF_3	121.6	121.6
CH_3	124.0	124.0
CH_2Cl	123.2	123.1
CH_2F	122.9	123.1
$CHCl_2$	122.9	122.9
CHF_2	122.1	122.2
CHClF	122.7	122.5
r	0.988	

The ^{13}C chemical shifts are correlated with seven explanatory variables by multiple regression analysis, which gives Eq. (3), in which n(H–H), n(H–Cl), n(H–F), n(F–F), n(F–Cl), n(Cl–Cl) are the average numbers of pairs of atoms gauche to the chlorodifluoromethyl group in $CClF_2$-CF_2-CXYZ, and n(C–C–C) is the average carbon frame angle (C–C–C angle) of $CClF_2$-CF_2-CXYZ.

$$\begin{aligned}\delta_C(CClF_2) = &-324.54n(F-F)-323.87n(Cl-Cl)\\ &-323.53n(H-F)-323.15n(Cl-F)\\ &-323.02n(H-Cl)-321.59n(H-H)\\ &+0.379n(C-C-C) \qquad (3)\end{aligned}$$

The relationships between the observed and calculated ^{13}C chemical shifts are shown in Table 5.

The regression coefficients in Eq. (3) are presumed to include the effect of magnetic anisotropy and the steric effect of the substituent R.

The substituent R containing many fluorine or chlorine atoms at X and Y positions would decrease the ^{13}C chemical shift values through the magnetic anisotropy of the atoms, and the substituent R containing many chlorine atoms would increase the ^{13}C chemical shifts by the steric effect of R. It seems that the combination of these two effects makes it difficult to predict ^{13}C chemical shifts in general.

The ^{19}F and ^{13}C chemical shifts of the difluoromethylene group in halogenated propanes ($CClF_2$-CF_2-R) are given in Table 6 and a plot of the ^{19}F and ^{13}C chemical shifts is presented in Fig. 4.

As Fig. 4 indicates, the relation between the ^{19}F and ^{13}C chemical shifts of the difluoromethylene group seems to be

Table 6
^{19}F and ^{13}C chemical shifts of CF_2 in $CClF_2$-CF_2-R

R	CF_2 δ_F (ppm)	CF_2 δ_C (ppm)
CCl_3	−108.3	110.7
CCl_2F	−113.8	109.8
$CHCl_2$	−119.2	108.3
$CClF_2$	−125.6	107.6
CHClF	−107.3	117.3
CF_3	−116.8	113.9
CHF_2	−122.7	112.9
CH_2Cl	−116.4	112.0
CH_2F	−129.3	109.3
CH_3	−123.3	110.5

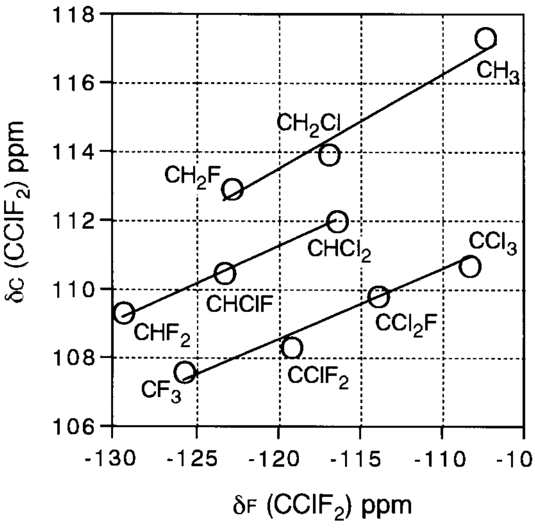

Fig. 4. Correlation between ^{19}F and ^{13}C chemical shifts of CF_2 in $CClF_2CF_2$-R.

Table 7
The number of H, Cl, F atoms in R, the average C–C–C angle of $CClF_2$-CF_2-R, and the observed and calculated ^{13}C chemical shifts of CF_2 in $CClF_2$-CF_2-R

CXYZ	Number of H, Cl, F atoms in R			C–C–C angle (deg)	δ_C (CF_2)	
	n(H)	n(F)	n(Cl)		obs.	calc.
CCl_3	0	0	3	117.21	110.7	111.0
CCl_2F	0	1	2	115.87	109.8	109.5
$CClF_2$	0	2	1	115.00	108.3	108.2
CF_3	0	3	0	114.41	107.6	107.1
CH_3	3	0	0	112.96	117.3	117.0
CH_2Cl	2	0	1	112.35	113.9	113.7
CH_2F	2	1	0	112.40	112.9	113.0
$CHCl_2$	1	0	2	114.03	112.0	111.9
CHF_2	1	2	0	113.58	109.3	110.2
CHClF	1	1	1	113.20	110.5	110.7
					$r=0.990$	

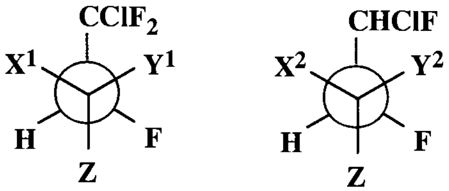

Fig. 5. Gauche positions (X^1, X^2, Y^1, Y^2) to the methyl group.

dependent on the number of hydrogen atoms in the substituted methyl group. The ^{13}C chemical shifts of the difluoromethylene group in $CClF_2$-CF_2-R are, therefore, expressed in Eq. (4), where n(H) is the number of hydrogen atoms in R:

$$\delta_C(CF_2) = 0.167\delta F(CF_2) + 2.29n(H) + 128.70 \qquad (4)$$

We assumed that the inductive effect of the substituent R and the distortion of electron clouds around the carbon atom are responsible for the ^{13}C chemical shifts of the difluoromethylene group in $CClF_2$-CF_2-R. As a result, the ^{13}C chemical shifts of the difluoromethylene group were successfully expressed by the number of H, Cl F atoms (n(H), n(F), n(Cl)) in R and the average carbon frame angle (C–C–C angle) of $CClF_2$-CF_2-R (n(C–C–C)). Table 7 shows n(H), n(F), n(Cl), n(C–C–C) and observed and calculated ^{13}C chemical shifts of the difluoromethylene group in $CClF_2$-CF_2-R.

$$\delta_C(CF_2) = 14.93n(H) + 12.03n(F) + 11.32n(Cl) + 0.639n(C-C-C) \qquad (5)$$

Although we reported [2] that the ^{19}F chemical shifts of the difluoromethylene group in 2,2-difluoropropanes are determined by magnetic anisotropy of atoms gauche to F in the difluoromethylene group, the ^{13}C chemical shifts of the difluoromethylene group in $CClF_2$-CF_2-R are affected by the inductive effect, or electronegativity of the substituent R. This may be because the carbon atom of the difluoromethylene group is linked to R by one σ bond, while the fluorine atom of the difluoromethylene group is two σ bonds distant.

2.3. ^{13}C NMR chemical shifts of diastereomers

We report the ^{13}C chemical shifts and the results of conformational analysis of diastereomers of 1,3-dichloro-1,1,2,3-tetrafluoropropane (234eb, [6]). Calculating the populations of rotamers on the basis of the differences in their heats of formation by AM1 [2], we figured the average number of pairs of atoms gauche to the terminal halogenated methyl group. As for $CClF_2$ in $CClF_2$-CHF-CX^1Y^1Z, gauche pairs of atoms are X^1–Y^1 = H–Cl, H–F, F–Cl; and as to CHClF in CX^2Y^2Z-CHF-CHClF, they are X^2–Y^2 = F–F, F–Cl (Fig. 5). The average carbon frame angles (C–C–C angles) of $CClF_2$-CHF-CHClF were also calculated as an indication of the steric interaction between $CClF_2$ and CHClF as listed in Table 8.

As we have already pointed out, both magnetic anisotropy of the atoms gauche to the terminal group and the steric effect of the terminal group are responsible for the ^{13}C chemical

Table 8
The average number of pairs of atoms gauche to the terminal methyl group, the calculated C–C–C angle of $CClF_2$-CHF-CHClF, and ^{13}C chemical shifts of $CClF_2$ and CHClF in diastereomers of $CClF_2$-CHF-CHClF

	Average number of pairs of atoms			C–C–C angle (deg)	δ_C
$CClF_2$	*n(H–Cl)*	*n(H–F)*	*n(Cl–F)*		*($CClF_2$)*
I	0.172	0.645	0.183	110.83	124.0
II	0.410	0.573	0.017	110.15	123.6
CHClF	*n(F–F)*	*n(Cl–F)*			*(CHClF)*
I	0.281	0.719		110.83	96.1
II	0.302	0.698		110.15	94.6

shift of a terminal halogenated methyl group in halogenated propanes. Eq. (3) shows that the pairs of atoms such as F–F and H–F decrease the ^{13}C chemical shift values of $CClF_2$ and CHClF. However, the larger the average C–C–C angle of halogenated propanes, the larger the ^{13}C chemical shift values of $CClF_2$ and CHClF. In $CClF_2$-CHF-CHClF, diastereomer I has a larger average C–C–C angle and more n(H–F) and n(Cl–F), while diastereomer II has more n(F–F), which makes the difference in the ^{13}C chemical shift values of $CClF_2$ smaller and that in CHClF larger.

3. Experimental details

3.1. NMR spectra

All the compounds were prepared as described in a previous paper [2]. The ^{19}F chemical shift data for halogenated propanes were extracted from the literature [2]. The ^{13}C NMR spectra were obtained in the pulse Fourier transform mode using a JNM-EX-90 (JEOL) instrument operating at 22.5 MHz. The spectral data were recorded in $CDCl_3$ solution (0.05–0.2 M) with TMS as an internal reference. Chemical shifts are given in parts per million (ppm) from TMS.

3.2. Calculations

MNDO calculations were performed on a Titan 3000 computer with full geometry optimization using a MOPAC 5.0 program [7–9].

3.3. Spectral data

1,1,1,3-Tetrachloro-2,2,3,3-tetrafluoropropane (214cb). ^{13}C NMR δ: 91.7 (tt, $^{2}J=34.2$, $^{3}J=2.8$ Hz); 110.7 (tt, $^{1}J=271$, $^{2}J=32.9$ Hz); 123.3 (tt, $^{1}J=304$, $^{2}J=38.8$ Hz) ppm.

1,1,3-Trichloro-1,2,2,3,3-pentafluoropropane (215ca). ^{13}C NMR δ: 122.8 (ttd, $^{1}J=302$, $^{2}J=37.4$, $^{3}J=2.2$ Hz); 109.8 (ttd, $^{1}J=270$, $^{2}J=33.9$, $^{2}J=31.3$ Hz); 114.2 (dtt, $^{1}J=305$, $^{2}J=34.6$, $^{3}J=2.2$ Hz) ppm.

1,3-Dichloro-1,1,2,2,3,3-hexafluoropropane (216ca). ^{13}C NMR δ: 122.1 (tt, $^{1}J=302$, $^{2}J=36.0$ Hz); 108.3 (t quint, $^{1}J=269$, $^{2}J=35.2$ Hz) ppm.

1-Chloro-1,1,2,2,3,3,3-heptafluoropropane (217ca). ^{13}C NMR δ: 117.9 (qt, $^{1}J=287$, $^{2}J=33.7$ Hz); 107.6 (tqt, $^{1}J=268$, $^{2}J=38.7$, $^{2}J=35.9$ Hz); 121.6 (tt, $^{1}J=299$, $^{2}J=34.5$ Hz) ppm.

1,1,2-Trichloro-2,3,3,3-tetrafluoropropane (224ba). ^{13}C NMR δ: 119.9 (qd, $^{1}J=287$, $^{2}J=30.8$ Hz); 105.5 (dq, $^{1}J=226$, $^{2}J=35.2$ Hz); 68.8 (d, $^{2}J=31.3$ Hz) ppm.

1,1,3-Trichloro-2,2,3,3-tetrafluoropropane (224ca). ^{13}C NMR δ: 122.9 (tt, $^{1}J=302$, $^{2}J=36.7$ Hz); 112.0 (tt, $^{1}J=264$, $^{2}J=31.9$ Hz); 65.4 (t, $^{2}J=30.8$ Hz) ppm.

1,1-Dichloro-2,2,3,3,3-pentafluoropropane (225ca). ^{13}C NMR δ: 64.9 (t, $^{2}J=30.2$ Hz); 110.9 (tq, $^{1}J=262$, $^{2}J=37.2$ Hz); 118.6 (tq, $^{1}J=287$, $^{2}J=35.2$ Hz) ppm.

1,3-Dichloro-1,1,2,2,3-pentafluoropropane (225cb). ^{13}C NMR δ: 122.7 (dt, $^{1}J=168$, $^{2}J=35.7$ Hz); 110.5 (dddd, $^{1}J=267$, $^{1}J=260$, $^{2}J=33.2$, $^{2}J=26.0$ Hz); 94.8 (ddd, $^{1}J=252$, $^{2}J=36.5$, $^{2}J=27.2$ Hz) ppm.

1-Chloro-1,1,2,2,3,3-hexafluoropropane (226cb). ^{13}C NMR δ: 122.1 (tt, $^{1}J=299$, $^{2}J=34.6$ Hz); 109.3 (ttt, $^{1}J=263$, $^{2}J=34.1$, $^{2}J=26.4$ Hz); 108.2 (tt, $^{1}J=254$, $^{2}J=32.1$ Hz) ppm.

1,1,2-Trichloro-3,3,3-trifluoropropane (233da). ^{13}C NMR δ: 122.0 (q, $^{1}J=281$ Hz); 63.1 (q, $^{2}J=32.6$ Hz); 67.4 (q, $^{3}J=1.9$ Hz) ppm.

1,3-Dichloro-1,1,2,2-tetrafluoropropane (234cc). ^{13}C NMR δ: 123.2 (tt, $^{1}J=299$, $^{2}J=36.5$ Hz); 113.9 (tt, $^{1}J=257$, $^{2}J=33.0$ Hz); 40.0 (t, $^{2}J=26.1$ Hz) ppm.

1,1-Dichloro-2,3,3,3-tetrafluoropropane (234ea). ^{13}C NMR δ: 120.9 (qd, $^{1}J=283$, $^{2}J=26.4$ Hz); 89.5 (dq, $^{1}J=201$, $^{2}J=33.9$ Hz); 64.7 (dq, $^{2}J=24.9$, $^{3}J=5.9$ Hz) ppm.

1,3-Dichloro-1,1,2,3-tetrafluoropropane, diastereomer I (234eb). ^{13}C NMR δ: 124.0 (td, $^{1}J=297$, $^{2}J=27.2$, $^{3}J=2.5$ Hz); 90.3 (ddt, $^{1}J=200$, $^{2}J=29.8$ Hz); 96.1 (ddt, $^{1}J=245$, $^{2}J=28.6$, $^{3}J=2.0$ Hz) ppm.

1,3-Dichloro-1,1,2,3-tetrafluoropropane, diastereomer II (234eb). ^{13}C NMR δ: 123.6 (tdd, $^{1}J=297$, $^{2}J=26.9$, $^{3}J=2.5$ Hz); 91.3 (dtd, $^{1}J=205$, $^{2}J=29.5$, $^{2}J=20.3$ Hz); 94.6 (ddt, $^{1}J=251$, $^{2}J=21.8$, $^{3}J=2.1$ Hz) ppm.

1-Chloro-1,1,2,2,3-pentafluoropropane (235cc). ^{13}C NMR δ: 122.9 (tt, $^{1}J=298$, $^{2}J=35.6$ Hz); 112.9 (ttd, $^{1}J=257$, $^{2}J=33.8$, $^{2}J=19.8$ Hz); 78.0 (dt, $^{1}J=186$, $^{2}J=30.5$ Hz) ppm.

1,1-Dichloro-3,3,3-trifluoropropane (243fa). ^{13}C NMR δ: 64.1 (q, $^{3}J=4.2$ Hz); 47.3 (q, $^{2}J=29.7$ Hz); 123.7 (q, $^{1}J=278$ Hz) ppm.

1-Chloro-1,1,2,2-tetrafluoropropane (244cc). ^{13}C NMR δ: 124.0 (ttt, $^{1}J=297$, $^{2}J=37.6$ Hz); 117.3 (tt, $^{1}J=251$, $^{2}J=34.1$ Hz); 17.7 (t, $^{2}J=24.7$ Hz) ppm.

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