^{13}C and ^{19}F NMR study of α,β-difluorostyryl derivatives of transition metal carbonylates. A method of signal assignment based on the carbon—fluorine spin-spin coupling constants

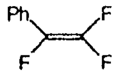
P. K. Sazonov,* M. M. Shtern, Yu. F. Oprunenko, and I. P. Beletskaya

Department of Chemistry, M. V. Lomonosov Moscow State University,
Leninskie Gory, 119899 Moscow, Russian Federation.
Fax: +7 (095) 932 8846. E-mail: Beletska@elorg1.chem.msu.su

The ^{13}C and ^{19}F NMR spectra of *Z*- and *E*-isomers of β-X-substituted α,β-difluorostyrenes (X = F, Cl, $CpFe(CO)_2$, $Re(CO)_5$, $Re_2(CO)_9Na$) were studied. Direct and long-range (across 1—5 bonds) spin-spin coupling constants and the ($^{13}C—^{12}C$) isotope shifts in the ^{19}F NMR spectra were determined. The study of the ^{13}C satellites in the ^{19}F NMR spectra of substituted difluorostyrenes permitted assignment of the ^{13}C NMR signals of the vinylic carbon atoms. Similarly, the signals in ^{19}F NMR spectra were assigned based on coupling constants of fluorine with *ipso*-carbon. These assignments were found to be in good agreement with the data available from the literature (X = F, Cl). The developed approach was applied to the elucidation of the structure of *Z*-$PhCF{=}CClFe(CO)_2Cp$.

Key words: σ-difluorostyryl complexes of transition metals, ^{13}C and ^{19}F NMR spectroscopy, spin-spin coupling constants of carbon with fluorine, ^{13}C satellites, signal assignment.

Previously[1—3] we have studied reactions of fluoroalkenes with anions of transition metal carbonyls. The interpretation of the ^{13}C and ^{19}F NMR spectra of *Z*- and *E*-β-X-substituted α,β-difluorostyrenes (X = F (**1**), Cl (**2**), $CpFe(CO)_2$ (**3**), $Re(CO)_5$ (**4**), $Re_2(CO)_9Na$ (**5**)) required reliable and justified assignment of signals to particular (α or β) fluorine or carbon atoms at the double bond. Another problem was to prove the structures of fluoro-derivatives, containing only one fluorine atom, for example, *Z*-$PhCF{=}CClFe(CO)_2Cp$ (**6**). At present, the commonest and the most direct method for solving these problems is heteronuclear correlation spectroscopy.[4] Since conventional NMR spectrometers are not usually adapted for the conduction of correlation experiments at two nuclei, in the present work, we made a detour based on analysis of ^{13}C satellites in the ^{19}F NMR spectra.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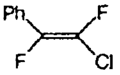
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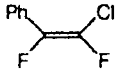
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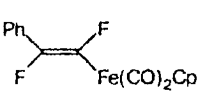
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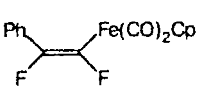
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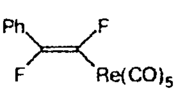
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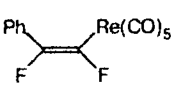
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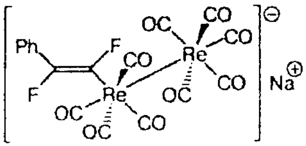
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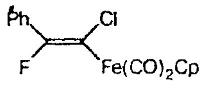
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The structures of carbonylate derivatives **3**—**5** were determined by mass spectrometry and ^{1}H (see Refs. 1, 3), ^{13}C, and ^{19}F NMR spectroscopy. The initial substrates **1**, *Z*-**2**, and *E*-**2** were also characterized by ^{13}C and ^{19}F NMR spectra; the ^{19}F NMR spectra of trifluorostyrene[5] and *Z*- and *E*-chlorodifluorostyrenes[6] and the ^{13}C NMR spectrum of trifluorostyrene[7] were consistent with the published data. The ^{13}C NMR spectra of *Z*- and *E*-isomers **2** are reported for the first time.

The few data concerning the spectra of σ-vinylic derivatives of carbonylates available from the literature[8—11] suggest that the low-field signal in the ^{19}F NMR spectra of the *Z*- and *E*-isomers of **3** and **4** and complex **5** belongs to the fluorine atom that occupies the geminal position in relation to the transition metal (Table 1). However, the fluorine chemical shifts, calculated for **3** and **4** by the additive scheme for the influence of substituents,[12] substantially deviate from the experimental values; this deviation can be as large as 10 ppm or higher. In addition, the original published data (the spectra of trifluorovinyl complexes of iron and rhenium carbonylates)[11] do not appear quite reliable, in particular, because the signal assignment was not sufficiently substantiated. Calculation of the chemical shift of fluorine in *Z*-$PhCF{=}CClFe(CO)_2Cp$ (**6**) by the method of

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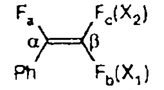
Table 1. Parameters of the ^{19}F NMR spectra of β-X-substituted α,β-difluorostyrenes



(**1—5**) and *Z*-$PhCF=CClFe(CO)_2Cp$ (**6**)[a]

Compound	δ			$^3J_{F,F}$/Hz	
	F_a	F_b	F_c	*trans*	*cis*
$PhCF=CF_2$[b] (**1**)	−175.27	−114.92	−100.60	109.5	32.6
Z-PhCF=CFCl (*Z*-**2**)	−145.95	−118.21	—	126.8	—
E-PhCF=CFCl (*E*-**2**)	−129.15	—	−102.85	—	10.8
Z-$PhCF=CFFe(CO)_2Cp$ (*Z*-**3**)	−145.77	−87.43	—	118.5	—
E-$PhCF=CFFe(CO)_2Cp$ (*E*-**3**)	−98.97	—	−71.12	—	~0[c]
Z-$PhCF=CFRe(CO)_5$ (*Z*-**4**)	−139.54	−99.55	—	114.8	—
E-$PhCF=CFRe(CO)_5$ (*E*-**4**)	−102.2	−81.8	—	—	10
Z-$PhCF=CFRe_2(CO)_9Na$ (**5**)[d]	−140.94	−88.16	—	114.2	—
Z-$PhCF=CClFe(CO)_2Cp$ (**6**)	−79.62	—	—	—	—

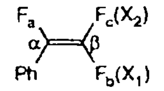
[a] C_6F_6 as the internal standard; chemical shifts were referred to $CFCl_3$, 25 °C, $(CD_3)_2CO$.

[b] $^2J_{F_c,F_b}$ = 74.7 Hz.

[c] No splitting was observed with a line half-width of 2—3 Hz.

[d] In THF-d_8 as the solvent.

Table 2. ^{13}C NMR chemical shifts (δ) in β-X-substituted α,β-difluorostyrenes



(**1—5**) and *Z*-$PhCF=CClFe(CO)_2Cp$ (**6**)[a]

Compound	C_α	C_β	C_{ipso}	C_o	C_m	C_p	C_{CO}	$C_{C_5H_5}$
$PhCF=CF_2$ (**1**)	129.77	154.82	127.82	125.34	129.72	130.06	—	—
Z-PhCF=CFCl (*Z*-**2**)	146.30	139.29	128.53	126.05	129.75	130.80	—	—
E-PhCF=CFCl (*E*-**2**)	143.63	137.82	128.20	127.94	129.56	131.15	—	—
Z-$PhCF=CFFe(CO)_2Cp$ (*Z*-**3**)	161.28	173.78	132.63	124.42	128.82	127.11	214.75	86.65
E-$PhCF=CFFe(CO)_2Cp$ (*E*-**3**)	152.95	162.09	134.48	130.52	128.82	128.90	214.55	87.99
Z-$PhCF=CFRe(CO)_5$ (*Z*-**4**)[b]	161.94	162.31	132.03	125.21	128.75	127.73	183.20 (ax); 181.77 (eq)	—
Z-$PhCF=CFRe_2(CO)_9Na$ (**5**)[b]	159.60	176.37	134.35	124.69	128.03	125.07	201.24; 199.9; 197.14; 192.24; 189.4	—
Z-$PhCF=CClFe(CO)_2Cp$ (**6**)[c]	163.00	125.16	134.34	128.88	128.47	128.51	216	87.5

[a] $(CD_3)_2CO$ as the solvent and the internal standard (δ 29.80), 25 °C.

[b] THF-d_8 as the solvent and the internal standard (δ 67.40, low-field signal).

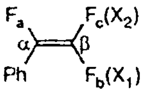
[c] In CD_2Cl_2 (CD_2Cl_2 as the standard, δ 53.8), δ: 162.15 (C_α); 124.32 (C_β); 214.39 (CO); 86.60 (C_5H_5).

increments does not make it possible to decide between different positions of the substituents at the double bond. The assignment of signals based on the ^{19}F NMR chemical shifts of carbonylate derivatives **3—5** is especially problematic in *E*-isomers in which the difference between the chemical shifts of the α- and β-fluorine atoms is somewhat greater than 20 ppm (see Table 1). Nevertheless, the *Z*- and *E*-configurations of compounds **3—5** can be identified quite reliably using the rule for the spin-spin coupling constants $^3J_{F,F_{cis}} \ll {}^3J_{F,F_{trans}}$, from which no exceptions have been observed so far.[13] It is of interest that the ^{19}F NMR spectrum of compound *E*-**3** consists of two singlets, and the line width at the half-height is ~2 Hz; in other words, the $^3J_{F,F}$ coupling constant was found to be close to zero.

The signals of the carbon atoms at the double bond in the ^{13}C {^{1}H} NMR spectra of compounds **1—5** (Tables 2, 3) can be easily detected based on the large magnitude[13—16] of the $^1J_{C,F}$ spin-spin coupling constant (> 200 Hz); however, it is much more difficult to attribute these signals to either α- or β-carbon atoms. The effect of β-substituents on the ^{13}C chemical shifts of the carbon atoms at the double bond in **1—6** is not additive; therefore, it provides little information for the assignment of signals. The replacement of the β-halogen atom by a transition metal results in a downfield shift of the signals of both carbon atoms; in compound *Z*-**4**, the chemical shifts of these atoms are almost identical (see Table 2).

We measured the $J_{C,F}$ constants not only in the ^{13}C NMR spectra but also in the ^{19}F NMR spectra while studying the ^{13}C satellites (Fig. 1); the resulting $J_{C,F}$ values were roughly equal (differed by < 1 Hz). The signals of the fluorine atoms, chemically bound to ^{13}C atoms, are somewhat shifted upfield; the values of the

Table 3. $^{13}C-^{19}F$ spin-spin coupling constants (J/Hz) in β-X-substituted α,β-difluorostyrenes



(**1**—**5**) and *Z*-PhCF=CClFe(CO)$_2$Cp (**6**)[a]

Carbon	**1**			*Z*-**2**[b]		*E*-**2**[b]		*Z*-**3**		*E*-**3**		*Z*-**4**[c]		**5**[c]		**6**,
atom	F_a	F_b	F_c	F_a	F_b	F_a	F_c	F_a	F_b	F_a	F_c	F_a	F_b	F_a	F_b	F_a
	Short-range constants ($^1J_{C,F}$, $^2J_{C,F}$, $^3J_{C_{ipso},F}$)															
C_α	226.0	45.5	19.6	235.6 (235.4)	43.5 (42.6)	244.9 (245.5)	18.8 (18.8)	203.5	39.3	248.6	15.3	205.4	36.4	199.9	40.9	221.1[d]
C_β	50.2	281.8	288.6	60.2 (59.8)	291.1 (292.8)	41.9 (41.8)	297.2 (299.5)	90.0	325.1	6.1	322.6	102.5	291.8	99.9	295.1	88.0
C_{ipso}	22.2	6.6 (d)		23.0 (23.7)	7.0 (6.7)	23.1 (23.1)	~0[e]	29.4	3.8	26.8	3.9	29.5	3.3	30.3	2.5	33.8
	Long-range constants ($^{3-5}J_{C,F}$)															
C_o	6.8, 5.9, 3.9			7.8, 6.4		5.2, 3.7		10.2, 7.4		2.8 (t)		10.4, 7.6		11.2, 7.7		4.4 (d)
C_m	2.0 (d)			1.8 (d)		~0[e]		2.5 (d)		~0[e]		2.7 (d)		3.0 (d)		~0[e]
C_p	1.9 (t)			1.9 (d)		1.7 (d)		2.2 (d)		2.2 (d)		2.4 (d)		2.3 (d)		<2
C_{CO}	—			—		—		5.5 (t)		7.0 (d)		4.8 (t, eq), 6.6, 2.4 (dd, ax)		9.5 (d), 6.8 (t), 4.5 (d)		5.8 (d)[d]

[a] $(CD_3)_2CO$ as the solvent, 25 °C.

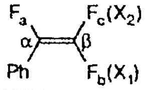
[b] The long-range $J_{C,F}$ constants were measured for a $CDCl_3$ solution. The short-range $J_{C,F}$ constants for the $CDCl_3$ solution are given in parentheses.

[c] THF-d_8 as the solvent.

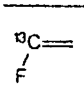
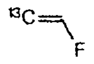
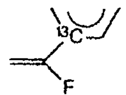
[d] CD_2Cl_2 as the solvent.

[e] No splitting was observed with a line half-width of ~1 Hz.

Table 4. Isotope chemical shifts (Δδ)[a] $^{12}C-^{13}C$ in the ^{19}F NMR spectra of β-X-substituted α,β-difluorostyrenes



(**1**—**4**) and *Z*-PhCF=CClFe(CO)$_2$Cp (**6**)[b]

Carbon	**1**			*Z*-**2**		*E*-**2**		*Z*-**3**		*E*-**3**		*Z*-**4**[c]		**6**,
atom	F_a	F_b	F_c	F_a	F_b	F_a	F_c	F_a	F_b	F_a	F_c	F_a	F_b	F_a
	0.083	0.094	0.093	0.085	0.102	0.084	0.105	0.080	0.076	0.098	0.084	0.082	0.076	0.097
	0.047	0.038	0.039	0.036	0.041	0.034	0.043	0.021	0.048	—	—	0.015	0.039	0.005
	0.0037	—	—	0.002	—	—	—	<0.005	—	<0.005	—	0.004	—	~0.001

[a] Upfield chemical shifts were taken to be positive.

[b] $(CD_3)_2CO$ as the solvent, 25 °C.

[c] THF-d_8 as the solvent.

($^{12}C-^{13}C$) isotope shifts[13] for compounds **1**—**4** and **6** are listed in Table 4. The effect of isotope substitution ($^{12}C-^{13}C$) is efficiently transferred by the π-bond, and the isotope shift of fluorine in the vicinal position to the ^{13}C atom is approximately half that observed in the case of direct coupling (see Table 4). Note that the signals of the =CFCl groups in the ^{19}F NMR spectra of *Z*- and *E*-chlorodifluorostyrenes undergo upfield isotope shifts ($^{35}Cl-^{37}Cl$)[17,18] (Δδ = 0.005, Fig. 2).

The assignment of the signals corresponding to the aromatic ring in the ^{13}C NMR spectra of difluorostyrenes **1**—**5** is quite obvious. The only assumption needed for this purpose is that the spin-spin coupling with fluorine is more pronounced in the *ortho*-position than in the

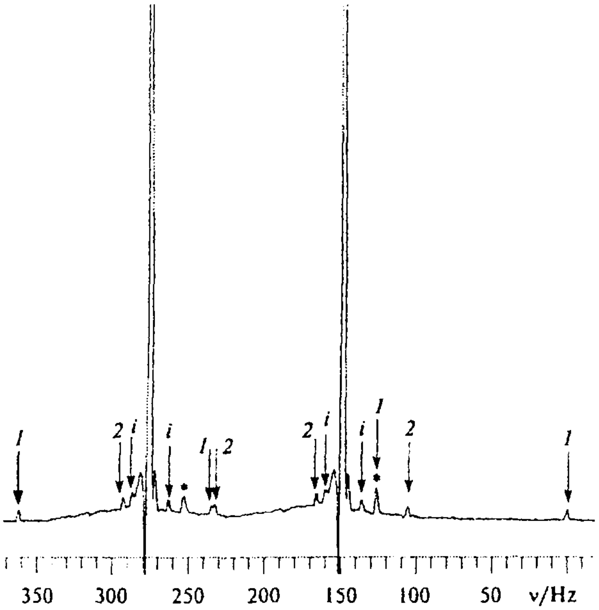


Fig. 1. Fragment of the ^{19}F NMR spectrum of *Z*-PhCF=CFCl (*Z*-2) corresponding to the =CFPh group. The satellites are denoted by: (*1*) $^1J_{C_\alpha,F}$, (*2*) $^2J_{C_\beta,F}$, and (*i*) $^2J_{C_i,F}$. The asterisk marks the side satellites due to rotation.

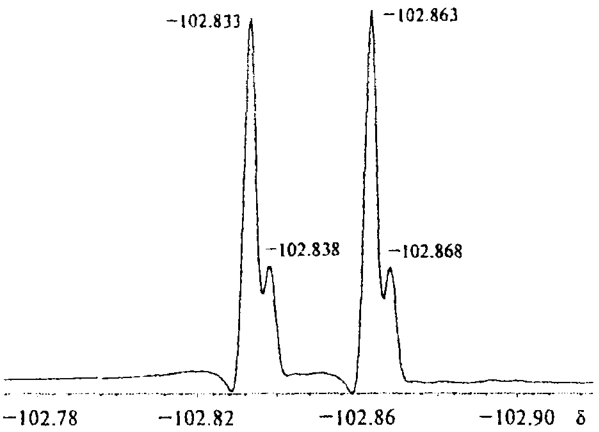
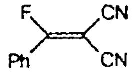


Fig. 2. Fragment of the ^{19}F NMR spectrum of *E*-PhCF=CFCl (*E*-2) corresponding to the =CFCl group.

meta- and *para*-positions (see Table 3). In fact, relatively large (> 5 Hz) $^nJ_{C,F}$ values (n > 4) were observed only in special cases.[14,15] The signal of the *ipso*-carbon atom (identified in the spectrum based on its low intensity or using the APT procedure) is split into a doublet of doublets in which the larger $J_{C,F}$ value varies in the 20—30 Hz range, while the smaller one is not greater than 7 Hz. In the case of the *Z*- and *E*-isomers of **2**, only the smaller constant depends on the geometric configuration (see Table 3).

In the spectra of fluorinated derivatives of various classes, $^2J_{C,F}$ are normally greater than $^nJ_{C,F}$ ($n \geq 3$) (with the same fluorine atom).[14,15] It can be assumed that in our case, too, the larger $J_{C_{ipso},F}$ refers to coupling across two bonds. Hence, the signal in the ^{19}F NMR spectrum, whose ^{13}C satellites exhibit a splitting equal to this constant, would belong to the α-fluorine atom (adjacent to the aromatic ring). Then the $^1J_{C,F}$ value observed for the ^{13}C satellites can be used to find the ^{13}C NMR signal corresponding to the carbon atom bound directly to this fluorine atom. Thus, a fairly strict assignment of signals becomes possible.

The validity of the initial assumption that for the *ipso*-carbon atom, $^2J_{C,F}$ is larger than $^3J_{C,F}$, can be verified most easily using the spectra of fluorostyrenes containing fluorine atom(s) in only one position at the double bond. We recorded the ^{13}C NMR spectrum for α-(fluorobenzylidene)malonodinitrile* (**7**), in which the $^2J_{C_{ipso},F}$ value is equal to 21 Hz. According to published data,[20] the $^2J_{C_{ipso},F}$ values for α-fluorostyrene derivatives **8** amount to 30—31 Hz. Conversely, in the case of fluorostyrenes **9** and **10**, $^3J_{C_{ipso},F}$ does not exceed[21,22] 9 Hz.



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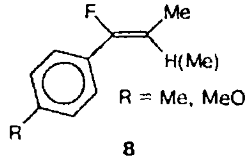

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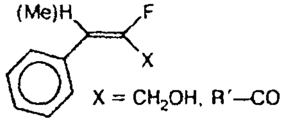

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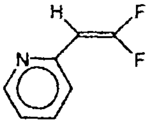

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For all the compounds studied here (**1**—**5**),** the larger $J_{C_{ipso},F}$ value corresponds to the ^{13}C satellites at the high-field signal in the ^{19}F NMR spectrum. For trifluorostyrene[5] and *Z*-chlorodifluorostyrene,[6] reliable assignment of the ^{19}F NMR signals can be found in the literature. According to these data, the higher-field signal belongs to the α-fluorine atom. In the case of trifluorostyrene, unambiguous assignment of signals of the =CF$_2$ and =CFPh groups in the ^{13}C NMR spectrum, and, hence, in the ^{19}F NMR spectrum can be performed based only on $^1J_{C,F}$, and this confirms the published data.

Thus, coupling of the *ipso*-carbon with the nearest fluorine atom is actually characterized by the larger of the two $J_{C,F}$ constants; this feature can serve as the basis for the assignment of signals.

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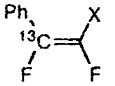
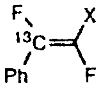
* The synthesis of 7 was described previously.[19]

** For *E*-3, we were not able to detect the ^{13}C satellites corresponding to the *ipso*-constant, because one of the components coincided with the main signal (^{12}C).

The approach to the interpretation of spectra proposed here makes it possible to discuss the behavior of $^2J_{C,F}$ in difluorostyrenes **1**—**5** (see below). It was found that $^2J_{C_\alpha,F}$ and, especially, $^2J_{C_\beta,F}$ values are sensitive to the geometric arrangement of electronegative substituents at the double bond: for *trans*-isomers, they are larger than for *cis*-isomers (see Table 3). Examples of similar geometric dependences of $^2J_{C,F}$ have been reported for some fluoroalkenes.[14] The position of $CpFe(CO)_2$ in the *Z*- and *E*-isomers of **3** has a much stronger effect on the magnitude of $^2J_{C_\beta,F}$ than the position of chlorine in the *Z*- and *E*-isomers of **2** ($^2J_{C_\beta,F}$ = 90 Hz for *Z*-**3**, $^2J_{C_\beta,F}$ = 6 Hz for *E*-**3**).

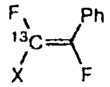


($^2J_{C,F}$ = 18±3 Hz)

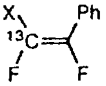


($^2J_{C,F}$ = 40±5 Hz)

X = F, Cl, $CpFe(CO)_2$, $Re(CO)_5$



($^2J_{C,F}$ > 50 Hz)



($^2J_{C,F}$ < 50 Hz)

X = $CpFe(CO)_2$, $Re(CO)_5$ X = $CpFe(CO)_2$

The results of this study can be used to elucidate the arrangement of substituents in monofluorostyrenes. Thus compound **6**, which is formally the product of replacement of the fluorine atom in styrene *E*-**2** under the action of iron carbonylate, $CpFe(CO)_2^-$, can be identified as *Z*-PhCF=CClFe(CO)$_2$Cp.[1] In fact, the fluorine atom in compound **6** occupies a geminal position in relation to the aromatic ring, because splitting of the signal corresponding to the *ipso*-carbon atom is typical of $^2J_{C_{ipso},F}$ (see Table 3). The *trans*-geometry of the double bond in **6** is indicated by the relatively large $^2J_{C_\beta,F}$ value, which is fairly close to that observed for *Z*-**3**, whereas the corresponding constant in *E*-**3** is smaller by an order of magnitude (see Table 3, Scheme 1).

Experimental

^{1}H, ^{13}C, and ^{19}F NMR were recorded on Varian VXR-300 and Varian VXR-400 spectrometers at 25 °C. The *Z*- and *E*-isomers of α,β-difluorostyrene derivatives of $CpFe(CO)_2$ (**3**) and $Re(CO)_5$ (**4**) were synthesized as described previously[1,3] from the corresponding carbonylates and α,β,β-trifluorostyrene (**1**) and *Z*- and *E*-β-chloro-α,β-difluorostyrene (**2**).

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