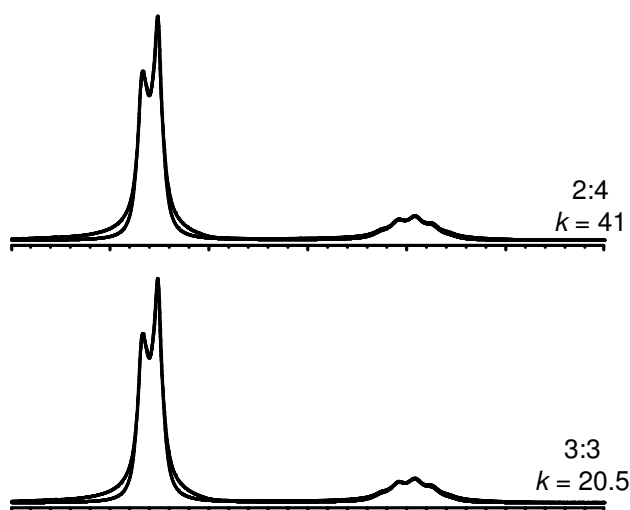


## Appendix I

For comparison between the two different mechanisms used to simulate the  $^{19}\text{F}$  NMR spectra of the samples studied, a series of rate values for  $\text{F}_5\text{W}(\text{OC}_6\text{F}_5)$  using the 2:4 mechanism and the Bailar twist are presented here, see table A.1. A comparison of the spectra obtained for one specific temperature can be seen in figure A.1.

**Table A.1.** Rate constants  $k$  ( $\text{sec}^{-1}$ ) obtained for  $\text{F}_5\text{W}(\text{OC}_6\text{F}_5)$  using two different mechanisms, 2:4 and Bailar twist.

Temperature ( $^{\circ}\text{C}$ )	Rate constant ( $k$ ) 2:4 mechanism	Rate constant ( $k$ ) Bailar mechanism
30	10.3	5.1
51	41.0	20.5
71	161.0	80.5
90	500.0	250.0
110	1290.0	645.0
130	3230.0	1615.0



**Figure A.1.** Simulated and experimental  $^{19}\text{F}$  NMR spectra of  $\text{F}_5\text{W}(\text{OC}_6\text{F}_5)$  at  $51^{\circ}\text{C}$  using two different mechanisms, 2:4 mechanism (upper), Bailar twist (lower).

## Appendix II

Linear regressions were carried out using the mathematical package “data analysis” from the program Microsoft Excel,<sup>®</sup> 2002. The confidential level of the linear regressions used was 95%. The input, as well as the output parameters for each of the compounds studied is presented here.

### i. $F_5W(OCH_2CF_3)$ in $C_2D_2Cl_4$

Temperature (K)	Temperature <sup>-1</sup> (K <sup>-1</sup> )	ln (k/T)
313.15	0.003193358	-4.086
323.15	0.003094538	-3.540
333.15	0.003001651	-2.989
343.15	0.002914177	-2.335
353.15	0.002831658	-1.791
373.15	0.002679887	-0.786
393.15	0.002543558	0.114

#### Regression Statistics

<b>Multiple R</b>	<b>0.999490266</b>
R Square	0.998980792
Adjusted R Square	0.998776951
Standard Error	0.052489261
Observations	7

	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%
<b>Intercept</b>	<b>16.76533623</b>	0.271662598	61.71381842	2.11432E-08	16.06700644	17.46366603	16.06700644	17.46366603
<b>X Variable 1</b>	<b>-6553.670663</b>	93.61649834	-70.00550948	1.1264E-08	-6794.31914	-6313.022186	-6794.31914	-6313.022186

### ii. $F_5Mo(OCH_2CF_3)$ in $C_2D_2Cl_4$

Temperature (K)	Temperature <sup>-1</sup> (K <sup>-1</sup> )	ln (k/T)
303.15	0.003298697	-2.142
313.15	0.003193358	-1.475
323.15	0.003094538	-0.851
333.15	0.003001651	-0.263
343.15	0.002914177	0.293
353.15	0.002831658	0.813
363.15	0.002753683	1.306

#### Regression Statistics

<b>Multiple R</b>	<b>0.999999652</b>
R Square	0.999999304
Adjusted R Square	0.999999165
Standard Error	0.001134223
Observations	7

	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%
<b>Intercept</b>	<b>18.72911562</b>	0.007124894	2628.687091	1.5122E-16	18.71080053	18.74743072	18.71080053	18.74743072
<b>X Variable 1</b>	<b>-6327.03749</b>	2.360795451	-2680.044765	1.37275E-16	-6333.106098	-6320.968882	-6333.106098	-6320.968882

iii.  $F_5W(OC_6F_5)$  in  $C_2D_2Cl_4$ 

Temperature (K)	Temperature <sup>-1</sup> (K <sup>-1</sup> )	ln (k/T)
303.15	0.003298697	-4.079
324.15	0.003084992	-2.761
344.15	0.002905710	-1.453
363.15	0.002753683	-0.373
383.15	0.002609944	0.521
403.15	0.002480466	1.388

Regression Statistics

Multiple R	<b>0.999675918</b>
R Square	0.999351941
Adjusted R Square	0.999189926
Standard Error	0.058465069
Observations	6

	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%
<b>Intercept</b>	<b>18.14533523</b>	0.246536022	73.60115196	2.04211E-07	17.46084008	18.82983038	17.46084008	18.82983038
<b>X Variable 1</b>	<b>-6748.740326</b>	85.92921224	-78.53837071	1.57527E-07	-6987.318561	-6510.162092	-6987.318561	-6510.162092

iv.  $F_5Mo(OC_6F_5)$  in  $C_2D_2Cl_4$ 

Temperature (K)	Temperature <sup>-1</sup> (K <sup>-1</sup> )	ln (k/T)
273.15	0.003660992	-0.704
278.15	0.003595182	-0.345
283.15	0.003531697	0.055
288.15	0.003470415	0.432
293.15	0.003411223	0.806
298.15	0.003354016	1.134
303.15	0.003298697	1.480
313.15	0.003193358	2.155
323.15	0.003094538	2.817
333.15	0.003001651	3.346

Regression Statistics

Multiple R	<b>0.999840711</b>
R Square	0.999681448
Adjusted R Square	0.999641629
Standard Error	0.025410911
Observations	10

	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%
<b>Intercept</b>	<b>21.98395273</b>	0.131936663	166.6250474	1.88298E-15	21.67970604	22.28819941	21.67970604	22.28819941
<b>X Variable 1</b>	<b>-6208.012302</b>	39.1802429	-158.4475195	2.81602E-15	-6298.362162	-6117.662441	-6298.362162	-6117.662441

v.  $F_5Mo(OC_6F_5)$  in  $CD_2Cl_2$ 

Temperature (K)	Temperature <sup>-1</sup> (K <sup>-1</sup> )	ln (k/T)
283.15	0.003531697	-0.402
288.15	0.003470415	-0.027
293.15	0.003411223	0.327
298.15	0.003354016	0.704
303.15	0.003298697	1.054

Regression Statistics

Multiple R	<b>0.99995929</b>
R Square	0.999918581
Adjusted R Square	0.999898226
Standard Error	0.00969455
Observations	6

	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%
<b>Intercept</b>	<b>21.63064821</b>	0.094687416	228.442693	2.20286E-09	21.36775325	21.89354317	21.36775325	21.89354317
<b>X Variable 1</b>	<b>-6240.366441</b>	28.15533157	-221.640666	2.48596E-09	-6318.538335	-6162.194546	-6318.538335	-6162.194546

vi.  $F_5Mo(OC(CF_3)_3)$  in  $C_2D_2Cl_4$ 

Temperature (K)	Temperature <sup>-1</sup> (K <sup>-1</sup> )	ln (k/T)
293.15	0.003411223	-7.939
303.15	0.003298697	-6.969
313.15	0.003193358	-6.085
333.15	0.003001651	-4.473
353.15	0.002831658	-3.210
363.15	0.002753683	-2.578
373.15	0.002679887	-2.101

Regression Statistics

Multiple R	<b>0.99954032</b>
R Square	0.999080851
Adjusted R Square	0.998897022
Standard Error	0.075554289
Observations	7

	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%
<b>Intercept</b>	<b>19.47189736</b>	0.330001813	59.00542534	2.6455E-08	18.62360208	20.32019264	18.62360208	20.32019264
<b>X Variable 1</b>	<b>-8014.0217</b>	108.7071442	-73.72120534	8.69933E-09	-8293.461854	-7734.581546	-8293.461854	-7734.581546