Electronic Supplementary Material (ESI) for Analyst

SUPPORTING INFORMATION

Quantitative solid-state Raman spectroscopic method for control of fungicides

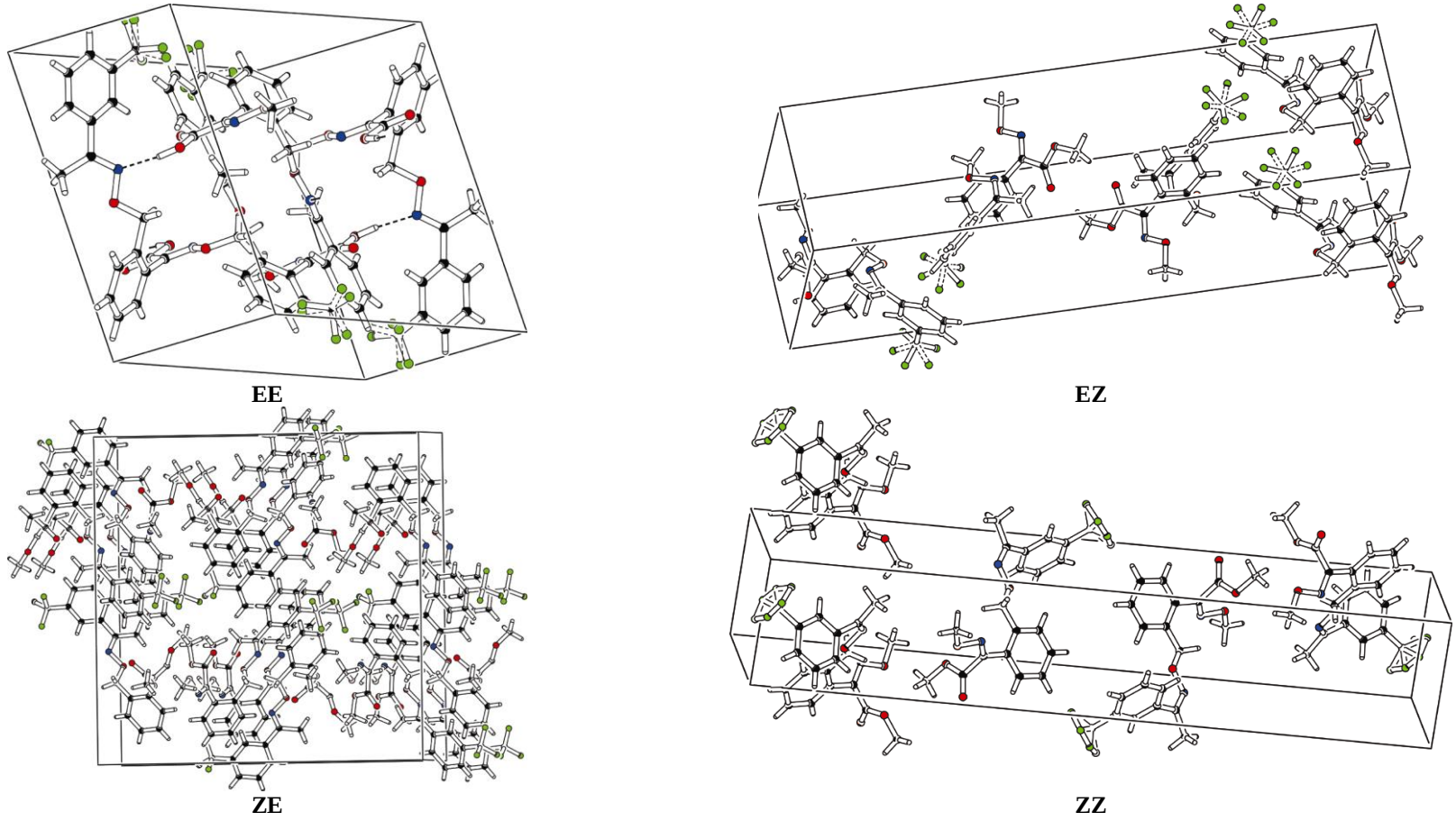
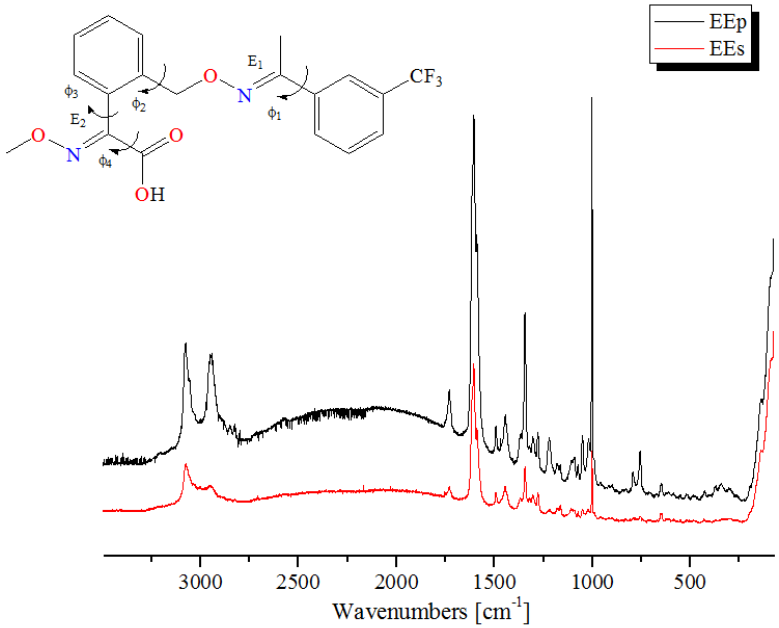
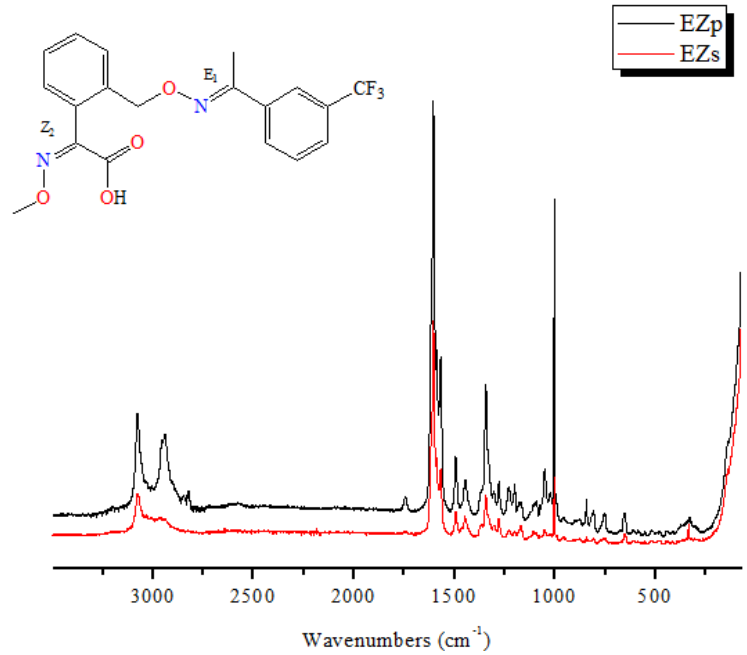
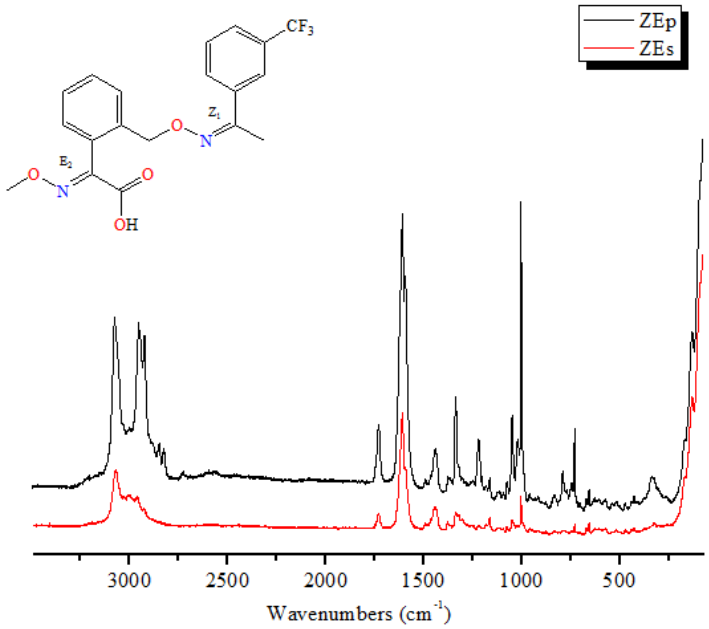
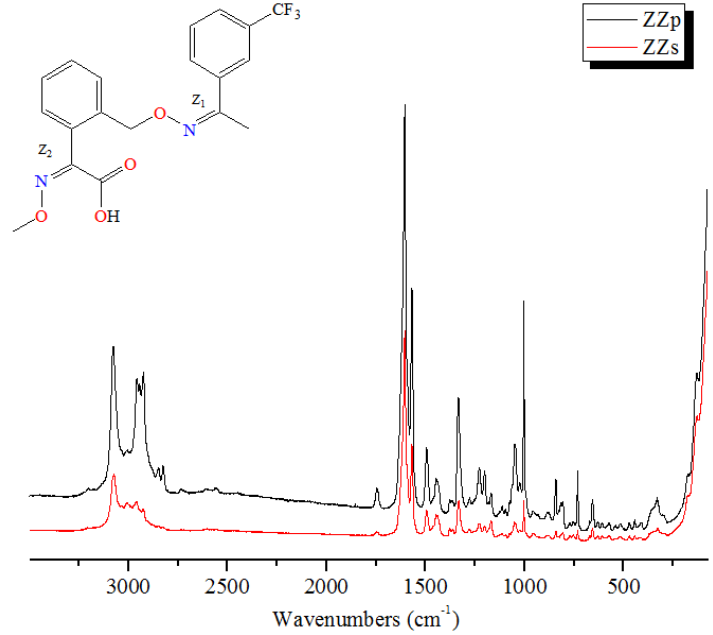


Figure S1. Crystal structures, hydrogen bonding and unit cell content of the acidic form of EE, and esters of EZ, ZE and ZZ, respectively [4c-f].









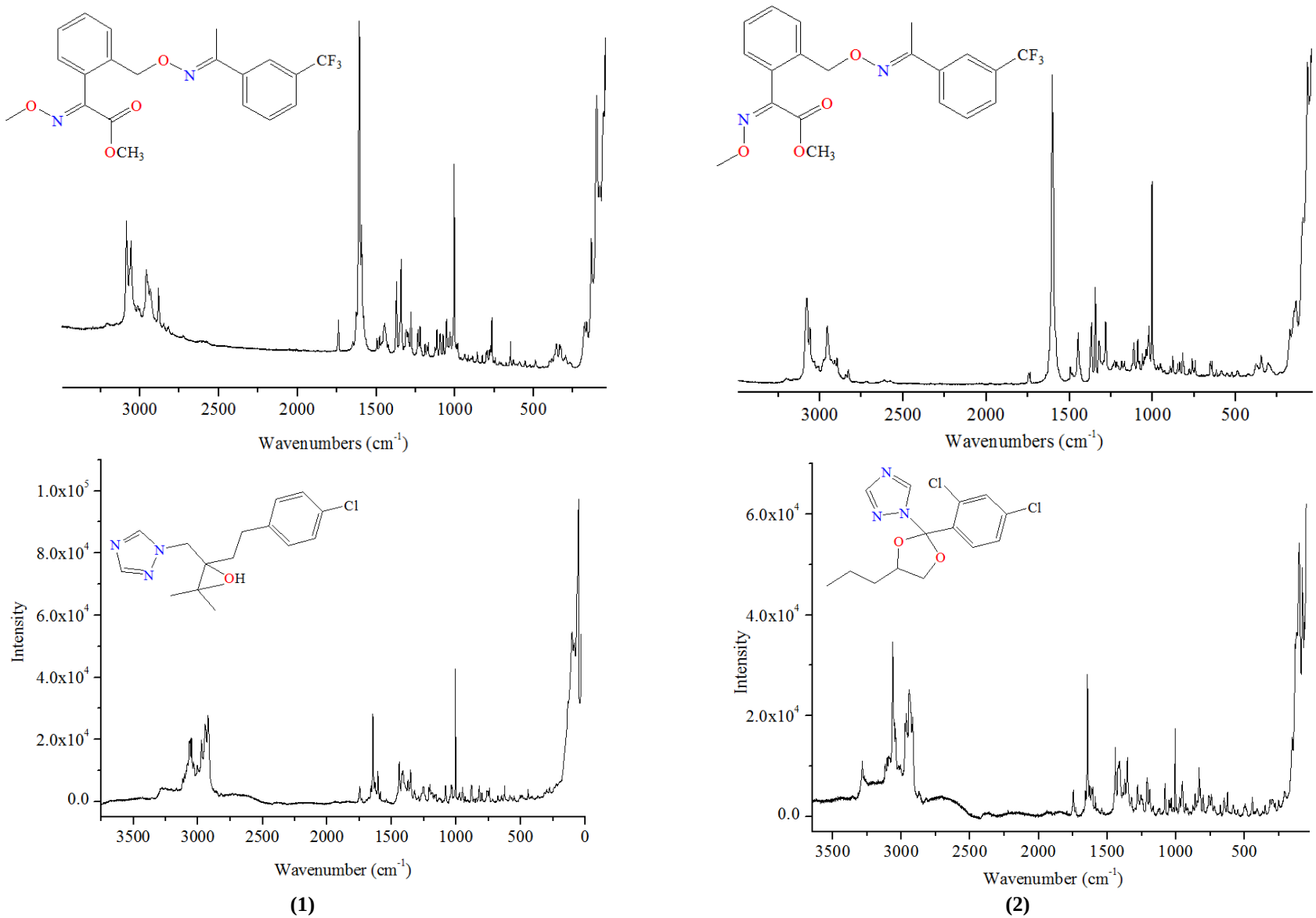


Figure S2. Chemical diagrams, parallel (p)/perpendicular (s) (acids) and subtracted (esters) solid-state Raman spectra of the four conformers EE, EZ, ZE and ZZ as acids and esters within 3500–40 cm^{-1}, tebuconazole (**1**), and propiconazole (**2**), respectively.

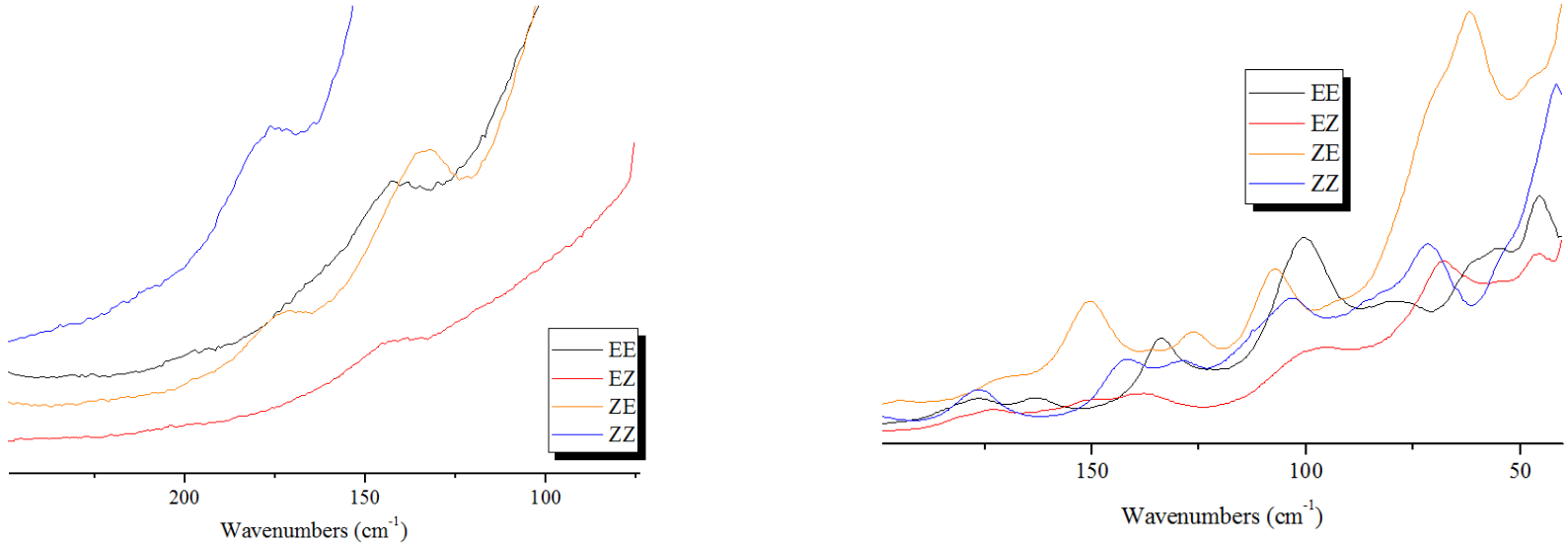


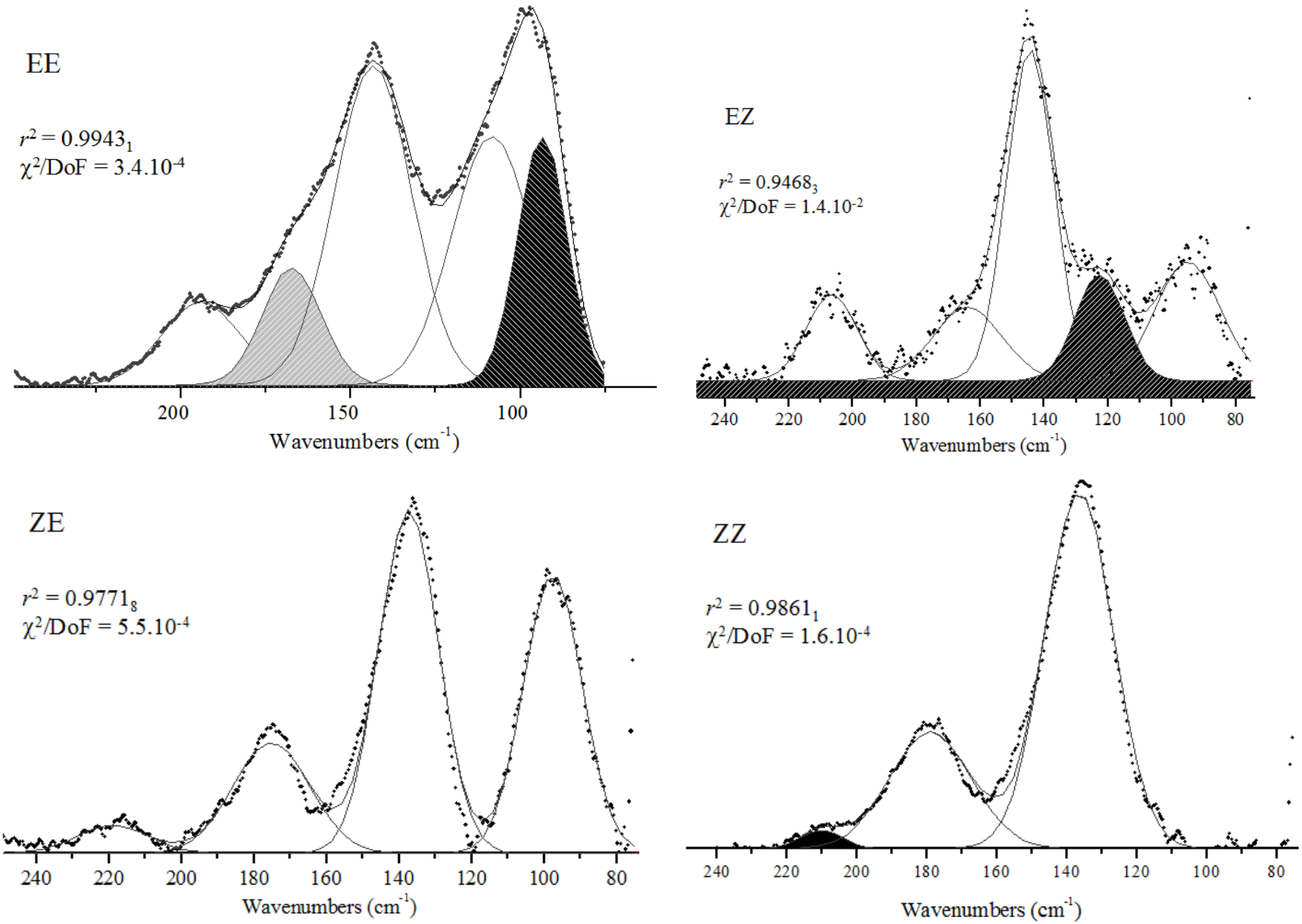
Figure S3. Experimental solid-state Raman spectra of acids (a) and esters (b) of EE, EZ, ZE and ZZ conformars within 250–30 cm^{-1} regions of the electromagnetic spectrum.

Table S1. Theoretical (M06-2X/ aug-cc-pVDZ) and experimental solid-state Raman spectra of the acids and esters of EE, EZ, ZE and ZZ, respectively; The frequencies are given in ν [cm^{-1} (THz)].

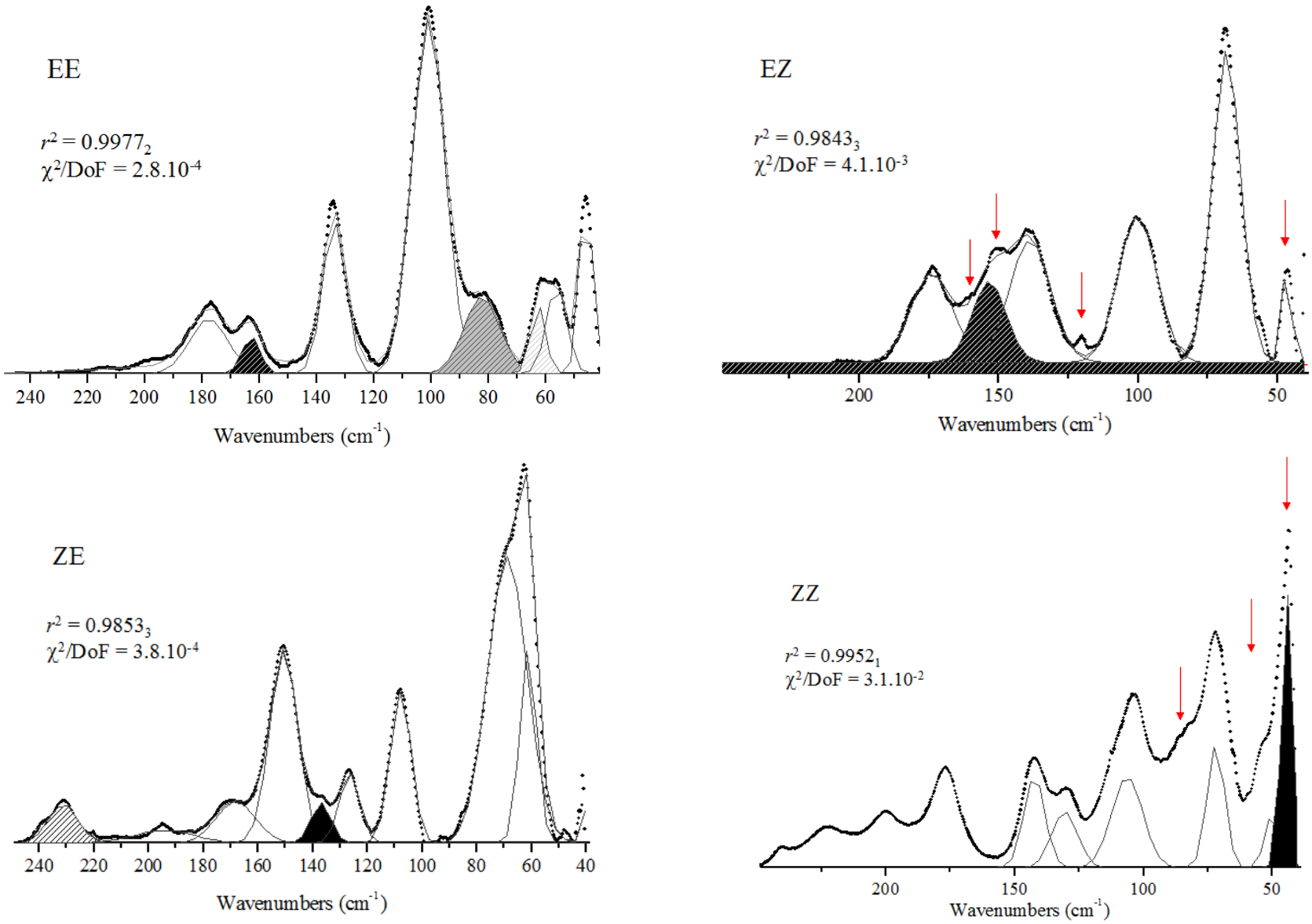
Assignment	**EE**				**EZ**				**ZE**				**ZZ**			
	Acids		**Esters**		**Acids**		**Esters**		**Acids**		**Esters**		**Acids**		**Esters**	
	Exp.	Theor.	Exp.	Theor.	Exp.	Theor.	Exp.	Theor.	Exp.	Theor.	Exp.		Exp.	Theor.	Exp.	Theor.
H-bond defformations	299 (8.97)	307 (9.21)			296 (8.88)	311 (9.33)			302 (9.06)	310 (9.30)			305 (9.15)	317 (9.51)		
ν^{as}_{CCl3}	263 (7.89)	263 (7.89)									**239 (7.17)**	244 (7.32)			240 (7.20)	248 (7.44)
											231 (6.93)	237 (7.11)			238 (7.14)	244 (7.32)
$\rho(CCl_3)$									219 (6.57)	220 (6.6)						
γ_{OCH3}					**206 (6.18)**	**205 (6.17)**									200 (6)	200 (6)
	195 (2.88)	195 (2.88)									**194 (5.82)**	195 (2.88)			188 (5.64)	188 (5.64)
Skeletal modes			**177 (5.31)**				**174 (5.22)**	177 (5.31)	**173 (5.19)**	174 (5.22)						
	165 (4.95)	164 (4.92)	162 (4.86)	163(4.89)	164 (4.89)						**168 (5.04)**	166 (4.96)	**180 (5.40)**	**180 (5.40)**		
							153 (4.59)	**155 (4.65)**			**150 (4.50)**	150 (4.50)				
	143 (4.29)	143 (4.29)	**133 (3.99)**	**132 (3.96)**	144 (4.32)		138 (4.14)	**140 (4.20)**	**137 (4.11)**	135 (4.05)	**137 (4.11)**	138 (4.14)	**138 (4.14)**	**140 (4.2)**	**142 (4.26)**	**141 (4.25)**
					122 (3.66)						**126 (3.78)**	125 (3.75)			**130 (3.9)**	**130 (3.9)**
	109 (3.27)	**109 (3.27)**	**100 (3)**	**100 (3)**			**100 (3)**	**100 (3)**			**107 (5.1)**	104 (3.12)			106 (3.18)	106 (3.17)
τ_{CH3}	**91 (2.73)**	90 (2.7)	**82 (2.46)**		94 (2.82)				**87 (2.61)**	88 (2.64)					78 (2.34)	78 (2.34)
torsion of			62 (1.86)	61 (1.86)			**68 (2.04)**	66 (1.98)			68 (2.04)	66 (1.98)				
entire side			56 (1.68)	55(1.67)							61 (1.86)	60 (1.8)				
chain about															49 (1.47)	50 (1.48)
the aromatic			45 (1.35)	45 (1.35)			**46 (1.38)**	44 (1.32)			41 (1.23)	40(1.22)			44 (1.32)	45 (1.35)
system																

Table S2. Hydrogen bonds and short contacts [Å], observed in the crystals of EE, EZ, ZE, and ZZ respectively [4].

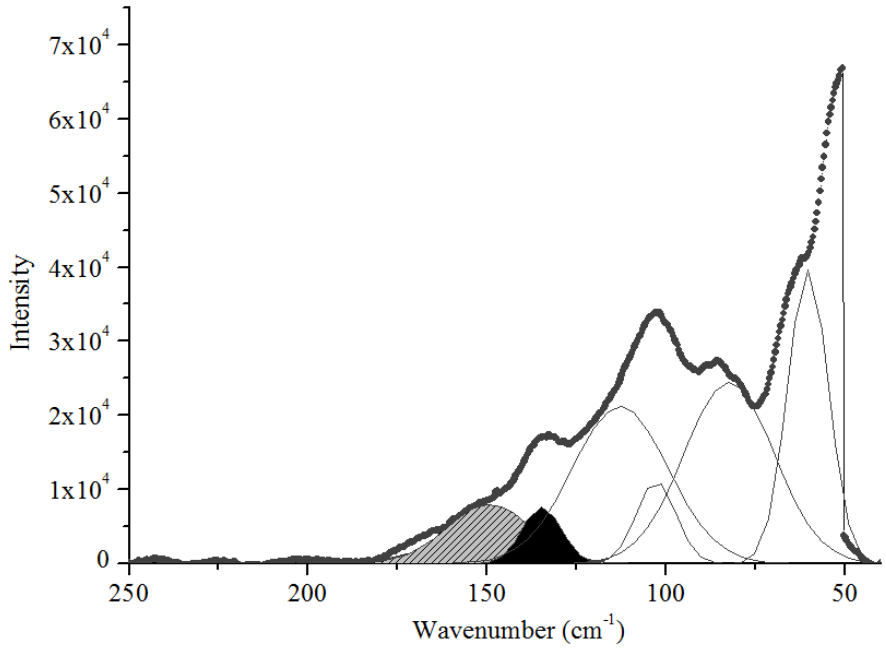
	EE		EZ		ZE		ZZ	
	Exp.	**Theor.**	**Exp.**	**Theor.**	**Exp.**	**Theor.**	**Exp.**	**Theor.**
OH···N	2.761	2.700						
CH···Cl	2.661	2.660	2.492	2.990			2.657	2.659
	2.645	2.658	2.359	2.350			2.632	2.634
			2.532	2.530				
Cl··Cl	2.830	2.830	2.395	2.394	2.798	2.798		



(a)



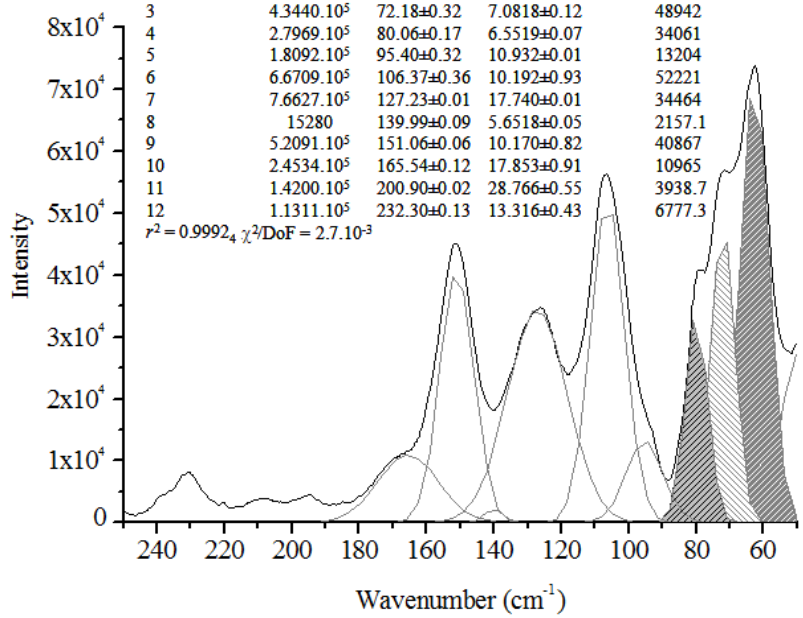
(b)



(c)

Peak	Area	Center	Width	Height
1	3.1796.10^5	50.14±0.02	9.3403±0.15	27161
2	7.6099.10^5	62.71±0.13	8.4812±0.37	71592
3	4.3440.10^5	72.18±0.32	7.0818±0.12	48942
4	2.7969.10^5	80.06±0.17	6.5519±0.07	34061
5	1.8092.10^5	95.40±0.32	10.932±0.01	13204
6	6.6709.10^5	106.37±0.36	10.192±0.93	52221
7	7.6627.10^5	127.23±0.01	17.740±0.01	34464
8	15280	139.99±0.09	5.6518±0.05	2157.1
9	5.2091.10^5	151.06±0.06	10.170±0.82	40867
10	2.4534.10^5	165.54±0.12	17.853±0.91	10965
11	1.4200.10^5	200.90±0.02	28.766±0.55	3938.7
12	1.1311.10^5	232.30±0.13	13.316±0.43	6777.3

$r^2 = 0.9992_4$ χ^2/DoF = 2.7.10^{-3}



(d)

Figure S4. Experimental solid-state Raman spectra within 250–50 cm^{-1} region of acids (a), esters (b), (1) (c) and mixture of (2) with EZ at molar ratio 1:8 (d), procedured with the baseline method; and non-linear curve-fitted pattern after the applied deconvolution method; non-linear multipeak Gaussian:Lorenzian mixed function 1:1 is uzed; *A*- total area under the curve from the baseline centre of the peak; w^2 "sigma", approximately 0.876 – 0.942 the FWHM; *w*/2 - is the standard deviation; The corresponding r^2 (χ^2/DaF) statistical values; The obtained quantities by the applied non-linear mathematical and statistical approaches were shown in (d), respectively. The data summarized in the (d) corresponded to three repeated measurements.

Table S3. Peak positions ni depending of the applied non-linear methods and smoothing procedures, using the SG and FFT as methods at different polynomial order (PO) and number of points (NP), respectively; In the SG method the number of points left/rigth is 16/16, respectively; The obtained data are after the three repeated measurements.

EE

Acids

FFT, NP=3	FFT, NP = 5	SG, PO = 2	SG, PO = 4
299±0.01$_1$	298±0.01$_2$	299±0.04$_4$	297±0.01$_1$
263±0.01$_6$	263±0.02$_2$	263± 0.02$_0$	261± 0.05$_5$
195±0.00$_3$	196±0.01$_3$	195 ± 0.07$_7$	197± 0.09$_3$
165±0.12$_1$	167±0.11$_0$	165 ± 0.10$_0$	166±0.12$_2$
143±0.11$_2$	144±0.11$_1$	143 ± 0.11$_0$	143 ± 0.11$_2$
109±0.019	110±0.02$_2$	109 ± 0.06$_9$	109 ± 0.09$_0$
91±0.24$_4$	90± 0.24$_1$	91 ± 0.09$_2$	93 ± 0.05$_5$

Ester

FFT, NP=3	**FFT, NP = 5**	**SG, PO = 2**	**SG, PO = 4**
177±0.55$_2$	178±0.18$_1$	177±0.02$_2$	177±0.12$_1$
162±0.11$_7$	161±0.01$_8$	162±0.01$_1$	161±0.01$_3$
133±0.33$_{26}$	133±0.13$_2$	133±0.11$_8$	133±0.10$_7$
100±0.03$_1$	101±0.01$_1$	100±0.11$_3$	100±0.01$_0$
82±0.02$_1$	82±0.01$_1$	82±0.01$_1$	82±0.01$_0$
62±0.02$_2$	62±0.01$_9$	62±0.01$_8$	62±0.01$_2$
56±0.06$_1$	56±0.07$_2$	56±0.07$_2$	56±0.05$_2$
45±0.00$_2$	45±0.02$_9$	45±0.00$_3$	45±0.00$_1$

EZ

Acids

FFT, NP=3	FFT, NP = 5	SG, PO = 2	SG, PO = 4
296± 0.73$_1$	295± 0.88$_7$	296±0.10$_3$	296±0.19$_8$
206 ± 0.05$_5$	205 ± 0.03$_9$	204±0.01$_2$	205±0.55$_8$
164 ± 0.09$_2$	163 ± 0.09$_1$	164±0.08$_2$	164±0.11$_9$
144 ± 0.78$_1$	144 ± 0.99$_9$	145±0.00$_2$	144±0.22
122 ± 0.00$_3$	121 ± 0.01$_1$	121±0.01$_1$	121±0.11$_1$
94 ± 0.099	95 ± 0.10$_0$	94±0.12$_6$	94±0.18$_0$

Ester

FFT, NP=3	**FFT, NP = 5**	**SG, PO = 2**	**SG, PO = 4**
174±0.11$_5$	174±0.00$_8$	174±0.02$_2$	174±0.00$_1$
153±0.17$_2$	153±0.07$_1$	153±0.01$_9$	153±0.09$_2$
138±0.11$_8$	138±0.00$_2$	138±0.01$_3$	138±0.00$_2$
100±0.17$_2$	100±0.03$_2$	100±0.00$_2$	100±0.01$_9$
68±0.11$_9$	68±0.00$_8$	68±0.00$_3$	68±0.00$_9$
46±0.10$_4$	46±0.00$_3$	46±0.00$_2$	46±0.01$_7$

ZE

Acids

FFT, NP=3	FFT, NP = 5	SG, PO = 2	SG, PO = 4
302±0.283$_3$	301±0.201$_7$	302±0.55$_1$	302±0.011$_1$
219±0.22$_9$	220±0.21$_8$	219±0.22$_7$	220±0.08$_9$
173±0.22$_2$	174±0.21$_7$	173±0.09$_3$	175±0.22$_8$
137±0.36$_7$	135±0.55$_9$	137±0.07$_8$	134±0.55$_2$
87±0.30$_3$	89±0.31$_3$	88±0.33$_1$	90±0.31$_2$

Ester

FFT, NP=3	**FFT, NP = 5**	**SG, PO = 2**	**SG, PO = 4**
239±0.28$_1$	239±0.03$_3$	239±0.01$_5$	239±0.03$_2$
231±0.12$_9$	231±0.01$_9$	231±0.01$_2$	231±0.10$_1$
194±0.04$_2$	194±0.03$_6$	194±0.03$_6$	194±0.01$_5$
168±0.01$_7$	168±0.20$_2$	168±0.01$_2$	168±0.01$_9$
150±0.05$_2$	150±0.55$_2$	150±0.05$_2$	150±0.05$_5$
137±0.01$_1$	137±0.08$_3$	137±0.01$_1$	137±0.01$_1$
126±0.01$_0$	126±0.01$_3$	126±0.01$_1$	126±0.01$_2$
107±0.21$_3$	107±0.41$_2$	107±0.11$_2$	107±0.01$_2$
68±0.02$_7$	68±0.05$_2$	68±0.03$_2$	68±0.04$_1$
61±0.10$_8$	61±0.55$_3$	61±0.10$_2$	61±0.01$_1$
41±0.60$_2$	41±0.66$_2$	41±0.66$_2$	41±0.21$_1$

ZZ

Acids

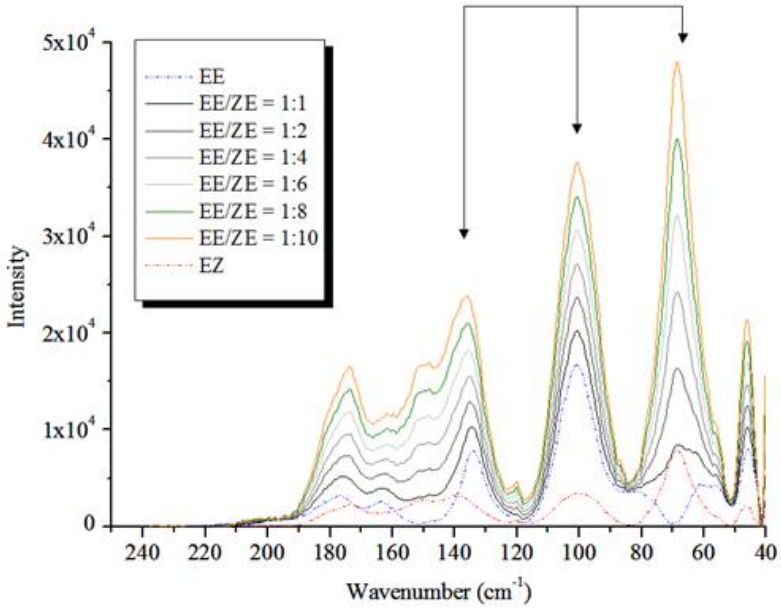
FFT, NP=3	FFT, NP = 5	SG, PO = 2	SG, PO = 4
305±0.008$_9$	306±0.075$_2$	305±0.509$_0$	306±0.188$_2$
180±0.077$_3$	181±0.076$_3$	180±0.00$_1$	182±0.076$_2$
138±0.010$_1$	134±0.012$_7$	138±0.617$_3$	135±0.012$_3$

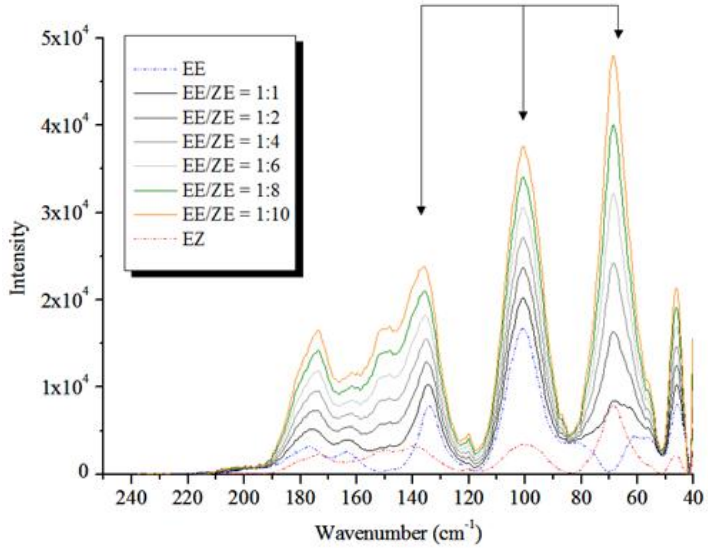
Ester

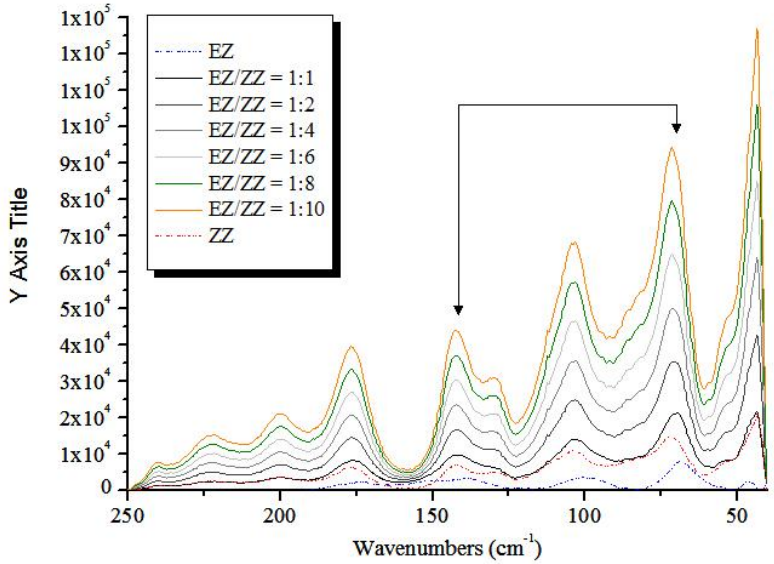
FFT, NP=3	**FFT, NP = 5**	**SG, PO = 2**	**SG, PO = 4**
240±0.01$_2$	240±0.01$_0$	240±0.01$_1$	240±0.01$_1$
238±0.02$_7$	238±0.01$_9$	238±0.01$_5$	238±0.01$_6$
200±0.03$_3$	200±0.01$_0$	200±0.01$_3$	200±0.01$_6$
188±0.01$_7$	188±0.01$_2$	188±0.01$_5$	188±0.01$_7$
142±0.01$_1$	142±0.01$_0$	142±0.01$_1$	142±0.01$_0$
130±0.01$_8$	130±0.01$_0$	130±0.01$_2$	130±0.01$_0$
106±0.01$_8$	106±0.01$_6$	106±0.01$_7$	106±0.01$_0$
78±0.09$_9$	78±0.01$_7$	78±0.05$_7$	78±0.00$_5$
49±0.09$_2$	49±0.03$_2$	49±0.06$_2$	49±0.00$_2$
44±0.01$_7$	44±0.01$_1$	44±0.00$_8$	44±0.01$_1$

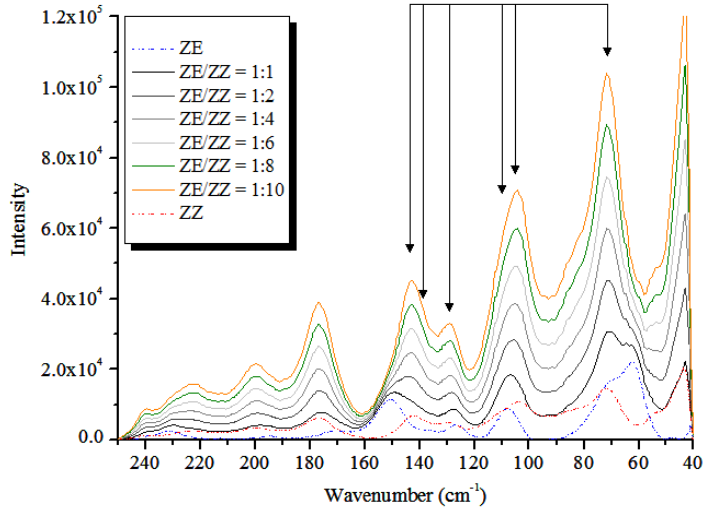
Table S4. Multiple Regression Analysis and ANOVA test the data in Table 3 for the $\nu_i^{(j)}$, FFT, N = 5 vs. SG., PO = 2 The Prob. F value for all calculations is <0.0001.

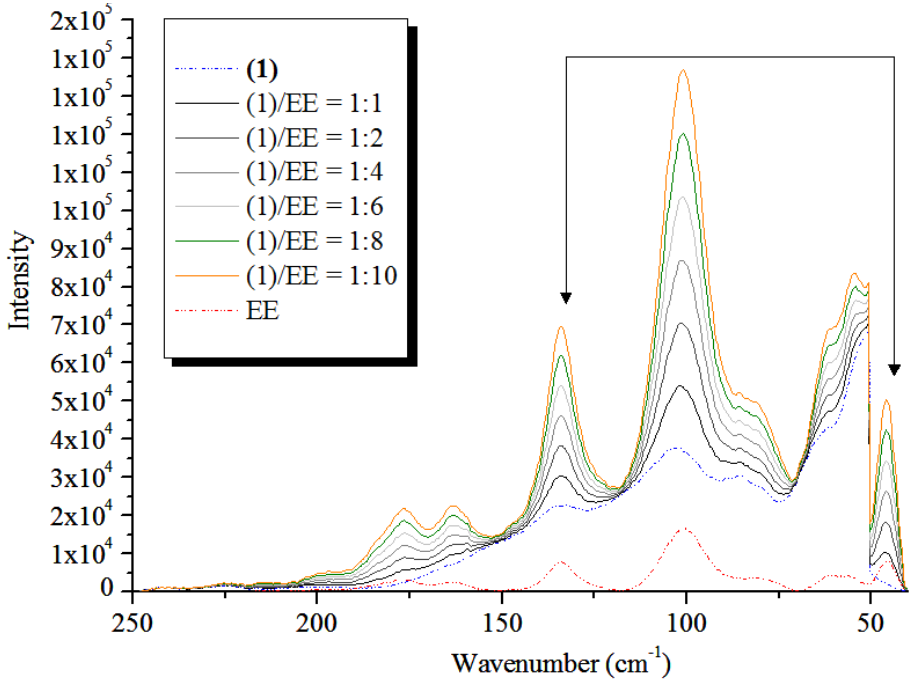
Value	**Std. Error**	**t-Value**	**Prob (>|t|)**	r^2	**ESD**		*df*	**SS**	**MS**	**F Statistic**	
Acids											**EE**
$1.31.10^{-12}$	$1.5.10^{-9}$	$8.6.10^{-4}$	0.9993_5	1	$1.3.10^{-9}$	Model	2	35827.4285_7	17913.7142_9	$9.8.10^{21}$	
$-1.8.10^{-12}$	$5.1.10^{-10}$	-0.0036_3	0.9972_8			Error	4	$7.3.10^{-18}$	$1.8.10^{-18}$		
1	$5.1.10^{-10}$	1.910_9	<0.0001			Total	6	35827.4285_7			
											EZ
-0.1318_3	0.7912_2	0.1666_2	0.8757_5	0.9999_2	0.8092_5	Model	2	31441.0947_7	15720.5473_8	24005.2380_1	
0.7150_2	0.3539_6	2.0200_5	0.1134_9			Error	4	2.6195_2	0.6548_8		
0.2888_9	0.3530_9	0.8181_7	0.459_2			Total	6	31443.7142_2			
											ZE
-0.68379	1.4985_7	1.4985_7	-0.456_3	0.9997_1	1.67876	Model	2	38736.4414_1	19368.220_7	6872.5014_2	
1.0051	0.0087_8	0.0087_8	114.463_5			Error	4	11.2728_8	2.8182_2		
$-6.9.10^{-4}$	0.0011_7	0.0011_7	-0.591_3			Total	6	38747.7142_9			
Esters											**EE**
$1.1.10^{-13}$	$1.2.10^{-10}$	$8.6.10^{-4}$	0.9993_4	1	$1.5.10^{-10}$	Model	2	17554.87_5	8777.437_5	$4.1.10^{-23}$	
$-1.7.10^{-12}$	$8.4.10^{-11}$	-0.0207_4	0.9842_6			Error	5	$1.1.10^{-19}$	$2.1.10^{-20}$		
1	$8.6.10^{-11}$	$1.1.10^{10}$	<0.0001			Total	7	17554.87_5			

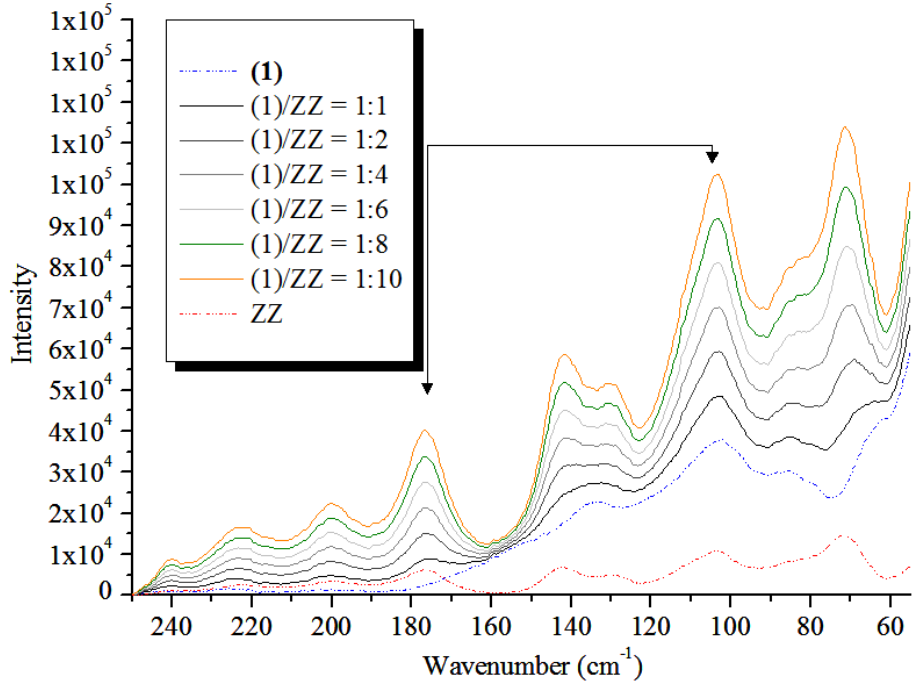


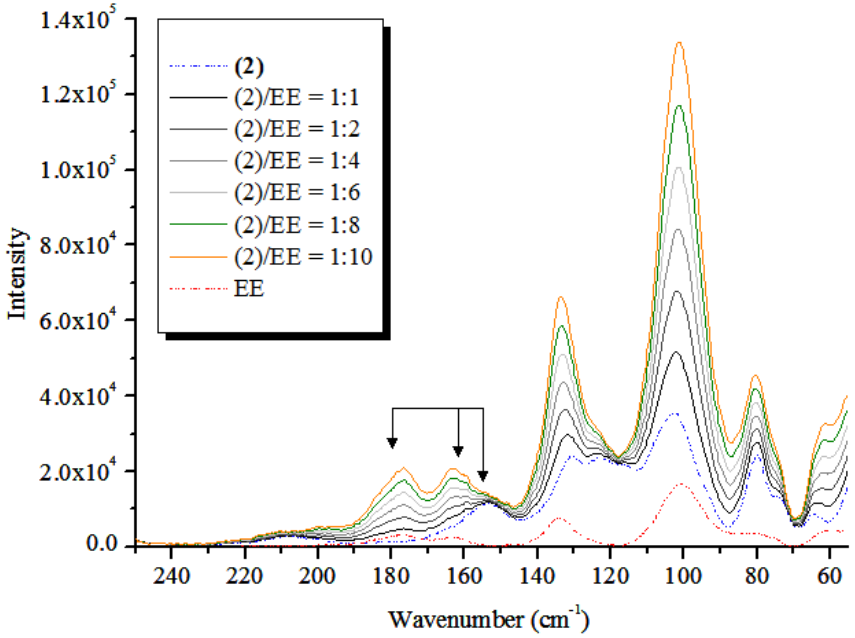


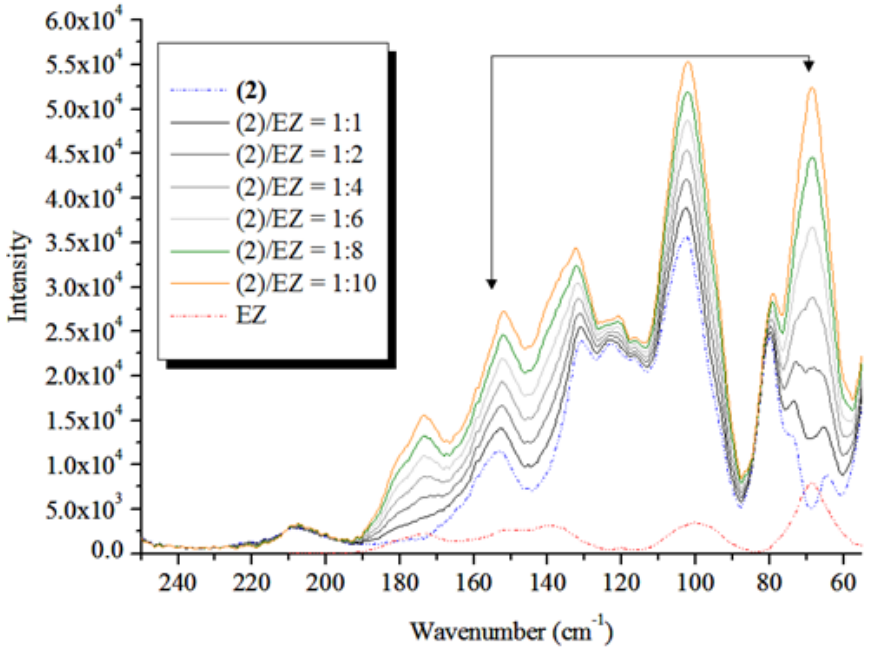












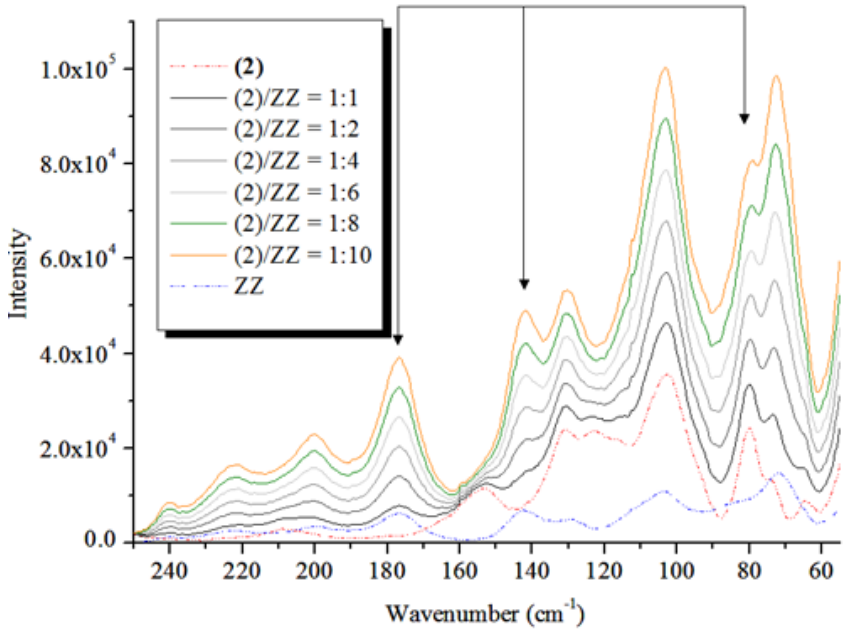
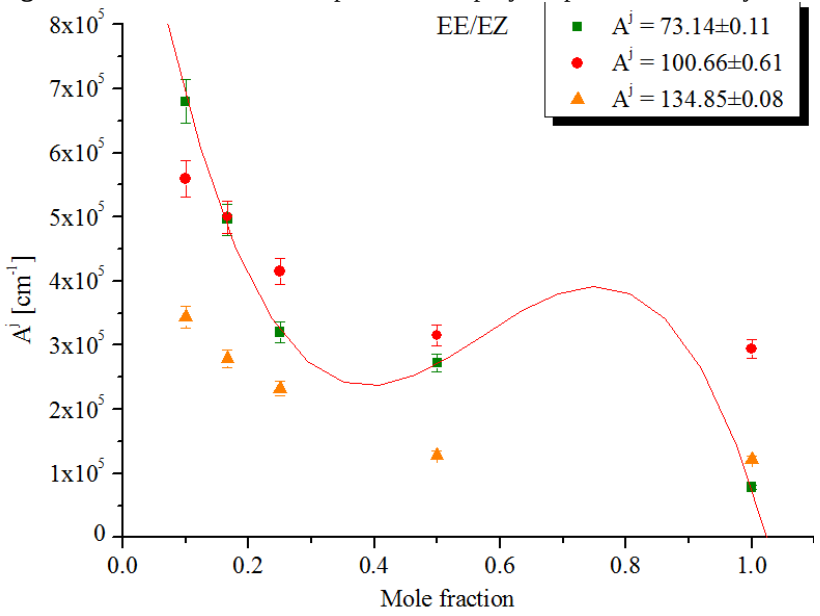
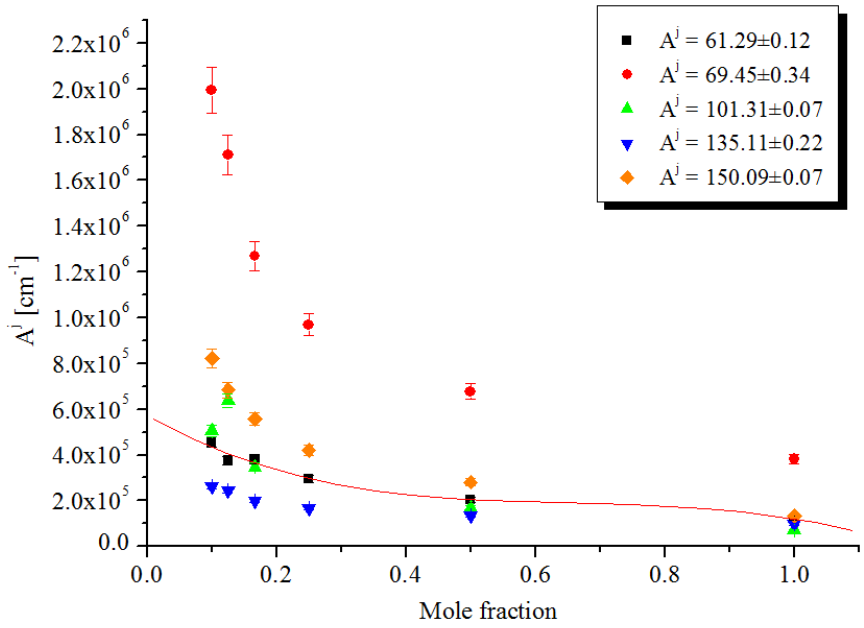


Figure S5. Solid-state Raman spectra of the polymorphs of the trifloxystrobin, tebuconazole **(1)** and propiconazole **(2)** in solid-mixtures ate different mole fractions.





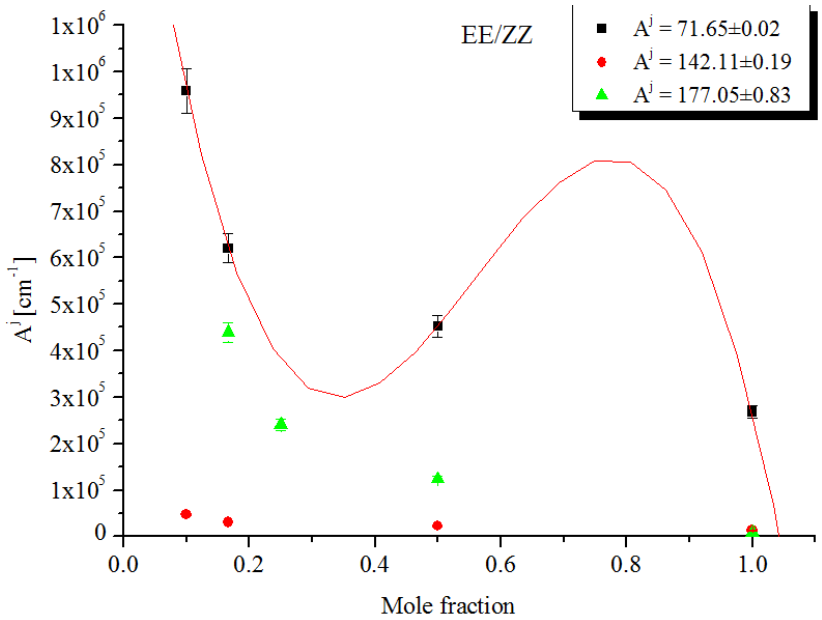


Figure S6. Quantitative dependences of the integral intensities as function of the concentration the analytes, using the selected set of the bands as shown; the standart deviations were obtained by the three consequently measured samples and three independent determinations of the shown quantities.