Olefin Polymerization Activity by Electronic Alteration on Proximate of Phenyl Phenoxy Ligand in Half-Metallocene Titanium(IV) Complexes.

Mateusz Brela, Artur Michalak
Department of Theoretical Chemistry,
Faculty of Chemistry,
Jagiellonian University,
Kraków, Poland

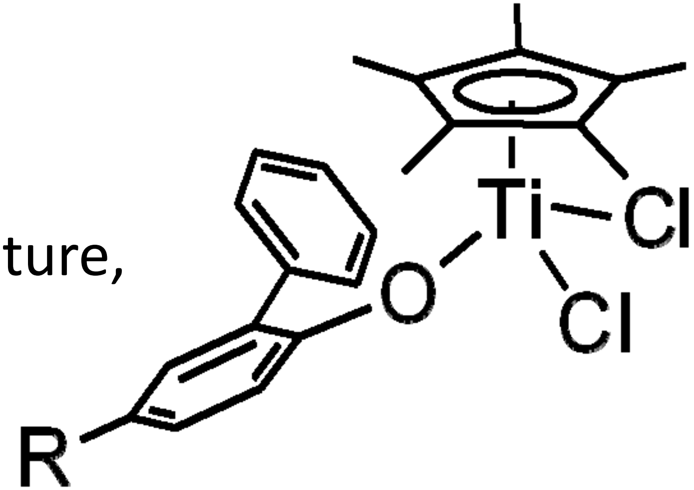
Zakopane, March 13th, 2014

Scope of the project

The substitution at the ligands is the main route used for modifying the properties of these complexes. Structural modifications:

-including steric tuning,

-changing the ligand backbone structure,



Presented research has been carried out in collaboration with the experimental groups from Korea University and SK Innovation Corp. (South Korea).

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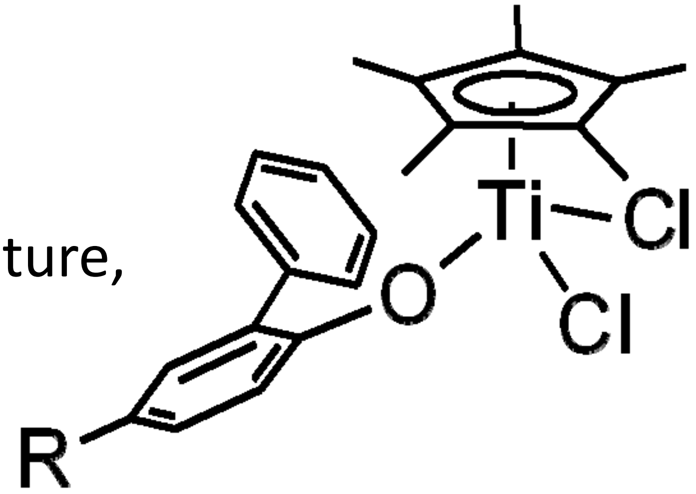

Ligand electronic effects
have been observed
***in many catalytic systems*.**

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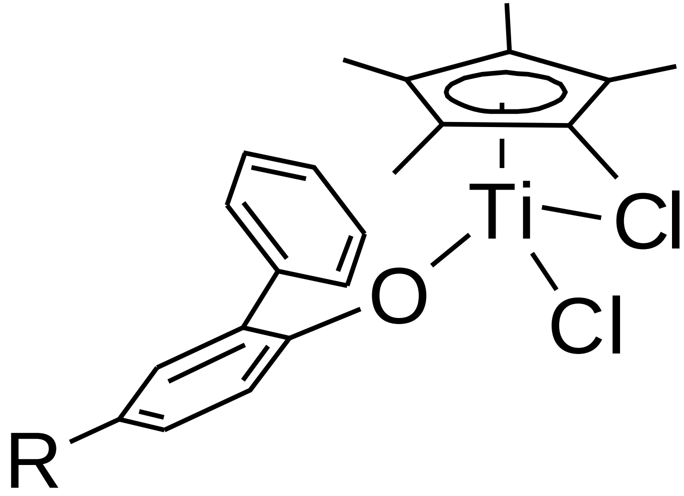
Main goal

The main goal of this study was to rationalize the experimental data concerning the activity of half-metallocene Titanium(IV) complexes by systematic, computational (DFT) studies.

In particular our study was focus on:

- influence of substituents on the Ti-O bonding, based on ETS-NOCV analysis;



R=F,Cl,H,C(CH$_3$)$_2$H,CH$_3$,C(CH$_3$)$_3$,OCH$_3$

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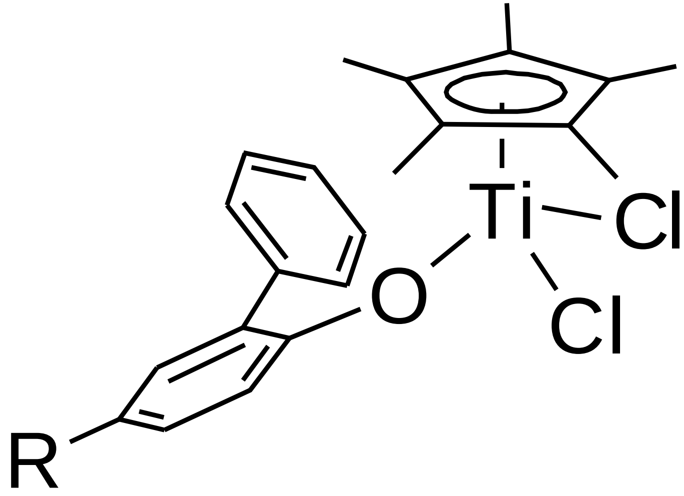

R=F,Cl,H,$C(CH_3)_2H$,CH_3,$C(CH_3)_3$,OCH_3

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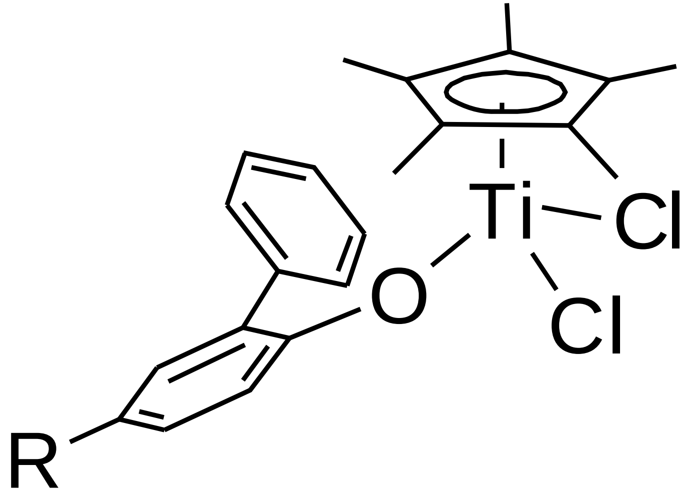
- understanding the preference of the alternative ethylene insertion pathways;
- rationalizing the differences in experimental activity.



R=F,Cl,H,C(CH$_3$)$_2$H,CH$_3$,C(CH$_3$)$_3$,OCH$_3$

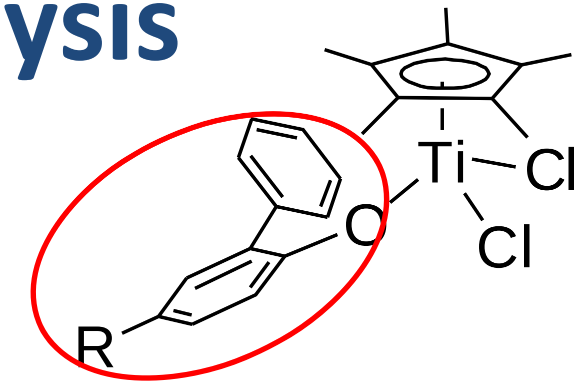
Computation

- Geometry optimization was performed for:
  - the titanium-based precatalysts;
  - cationic intermediates in the catalytic cycle: β-agostic alkyl complexes, ethylene π-complexes.
- The transition state optimization was carried out starting from the structures obtained from a series of constrained-optimizations with the particular C-C or C-H distance used as a respective reaction coordinate.
- The analysis of the titanium-oxygen and titanium-ethylene bonding was performed using ETS-NOCV approach [5].

Computational details

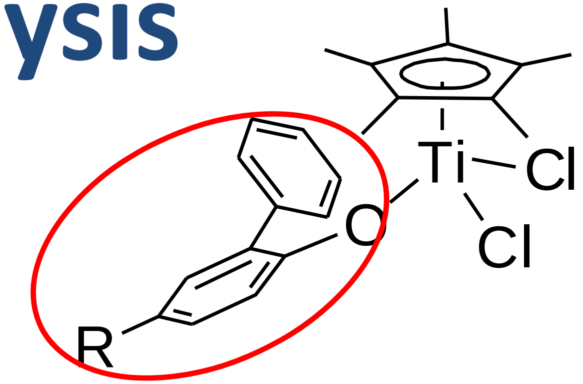
- ADF (Amsterdam Density functional) program, version 2010.02; DFT (Density Functional Theory) with Becke88/Pedrew86 exchange-correlation functional.
- A standard triple-ζ STO basis containing one set of polarization functions (TZP) was adopted for metal atoms, Ti.
- Standard double- ζ STO with one set of polarization functions (DZP) were used for the remaining elements (H, C, O, Cl and F).
- The 1s electrons of C, N, O, F as well as the 1s-2p electrons of Ti and Cl were treated as a frozen core.

Precatalyst analysis



	Decomposition scheme (ETS)					Hirshfeld Charge on Ti	Bond-Order Ti-O
	ΔE_{Pauli}	ΔE_{elstat}	ΔE_{steric}	ΔE_{orb}	$\Delta E_{bonding}$		
R=F	132,36	-257,82	-125,46	-157,84	-283,29	0,499	1,276
R=Cl	131,75	-253,65	-121,90	-157,65	-279,55	0,498	1,266
R=H	134,53	-261,95	-127,42	-159,61	-287,03	0,496	1,275
R=$C(CH_3)_2H$	136,54	-260,23	-123,68	-166,46	-290,14	0,490	1,292
R=CH_3	135,81	-261,48	-125,67	-164,14	-289,81	0,491	1,287
R=$C(CH_3)_3$	135,77	-259,90	-124,14	-165,67	-289,80	0,495	1,300
R=OCH_3	135,68	-263,07	-127,39	-166,40	-293,79	0,491	1,300

Precatalyst analysis



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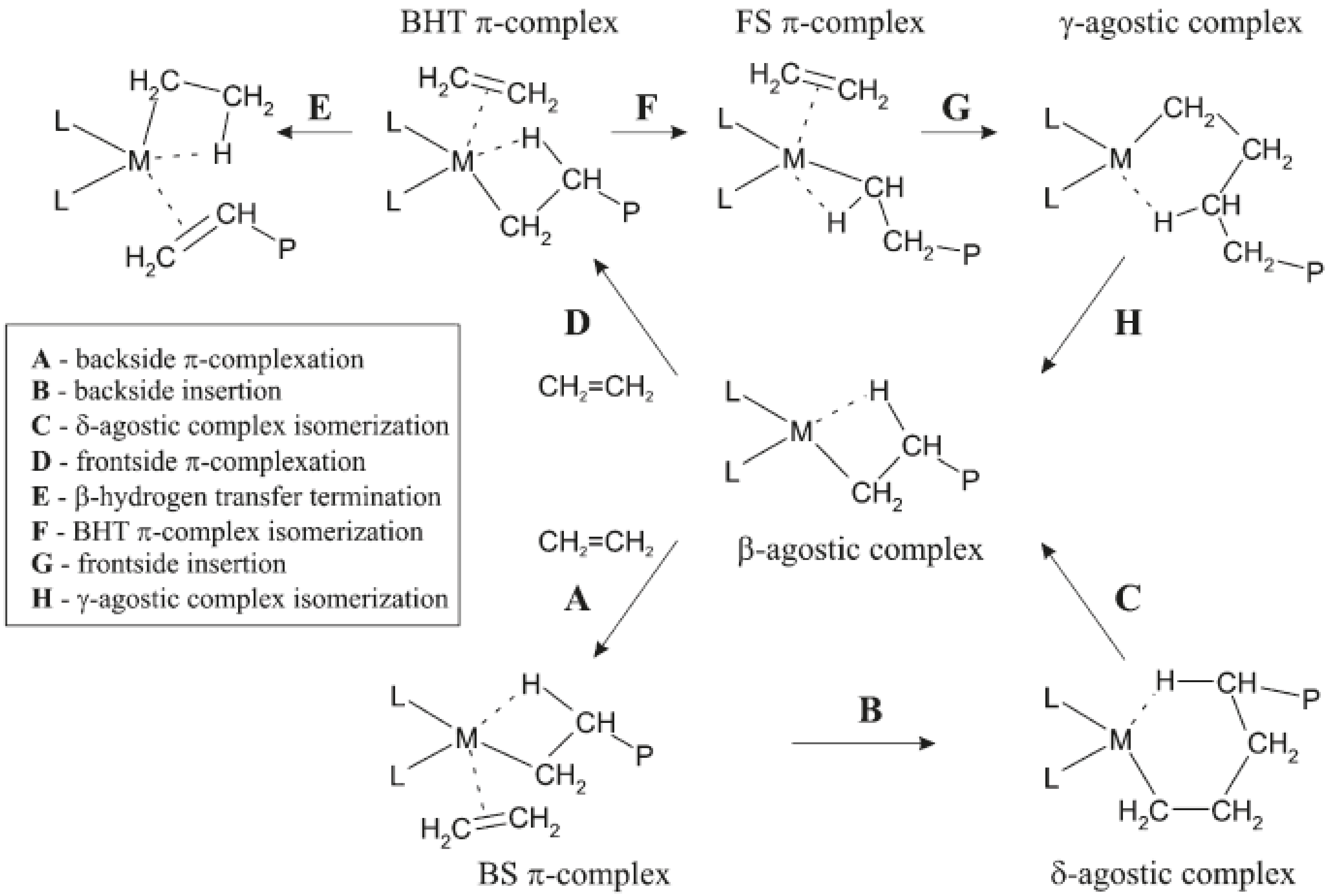
Correlation ?

Chain propagation reactions studied

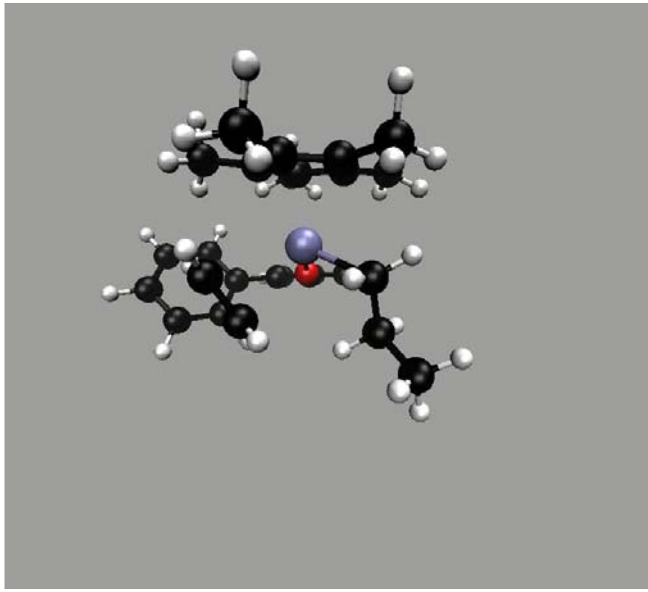


A - backside π-complexation
B - backside insertion
C - δ-agostic complex isomerization
D - frontside π-complexation
E - β-hydrogen transfer termination
F - BHT π-complex isomerization
G - frontside insertion
H - γ-agostic complex isomerization

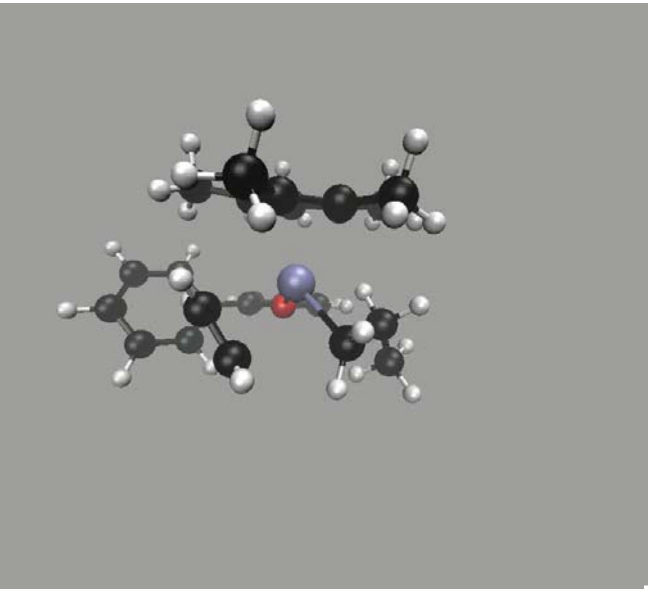
Alternative pathways for insertion of ethylene into propyl chain.

Organometallics, Vol. 29, No. 21, 2010, Srebro, M. et. al.

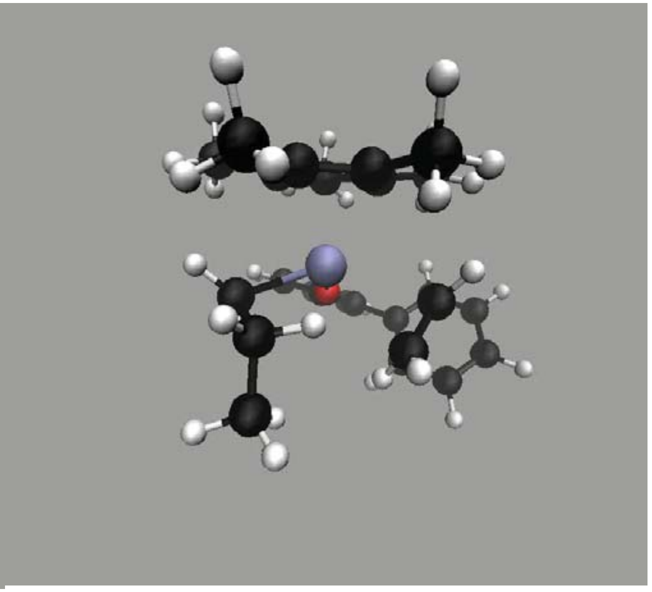
FS_syn



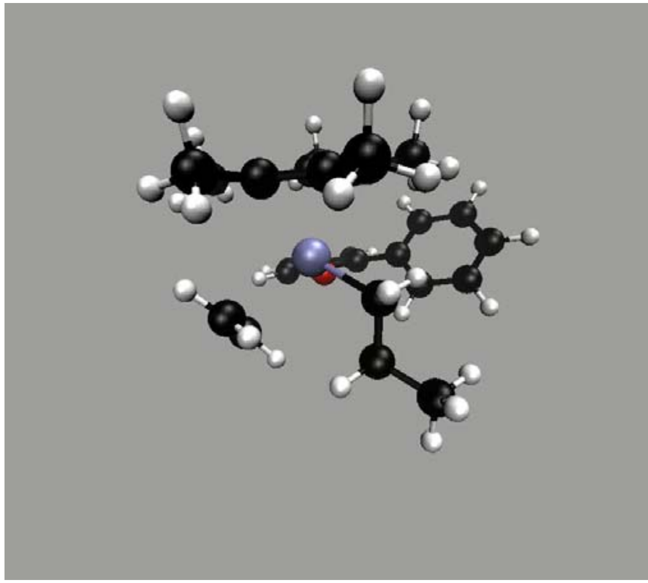
BS_syn



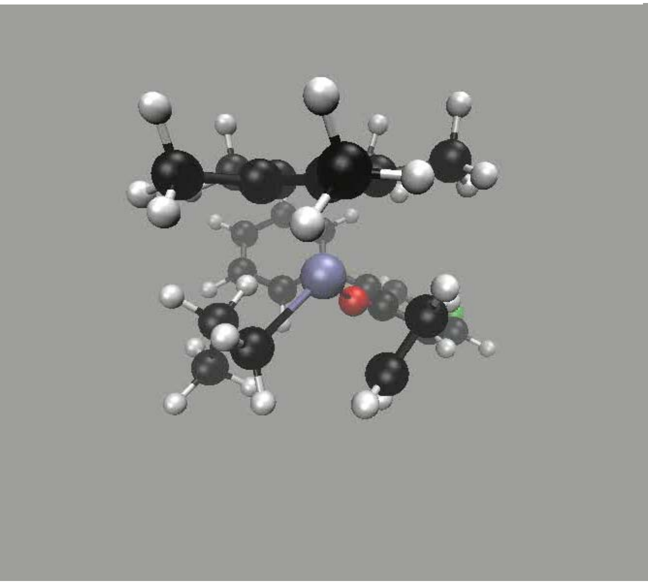
BHT_syn



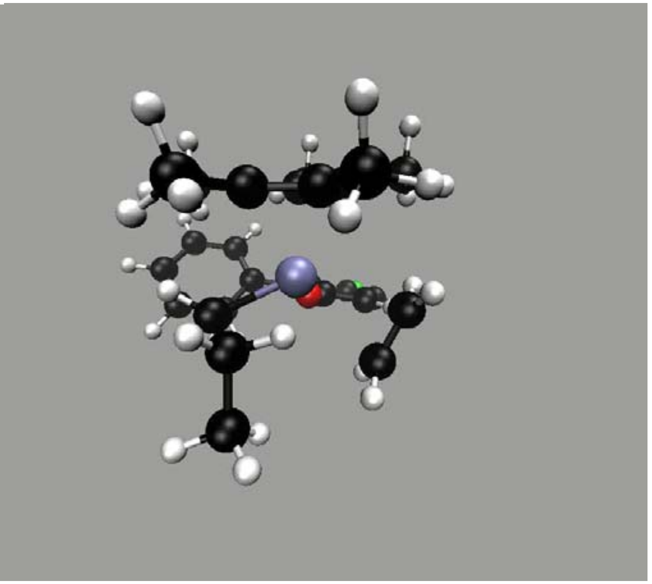
FS_anti



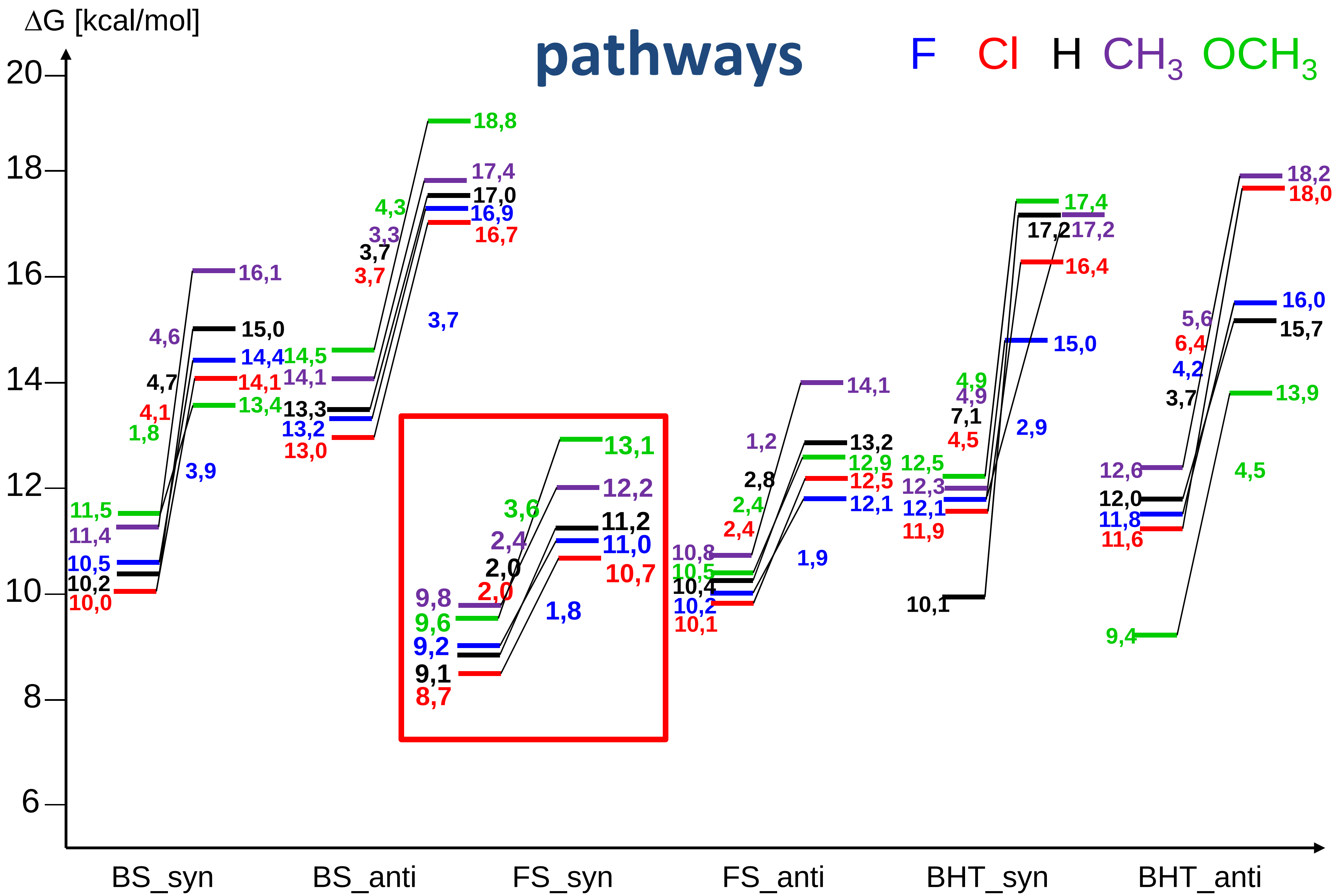
BS_anti



BHT_anti



Activation barier for alternative pathways



Theoretical activity parameter

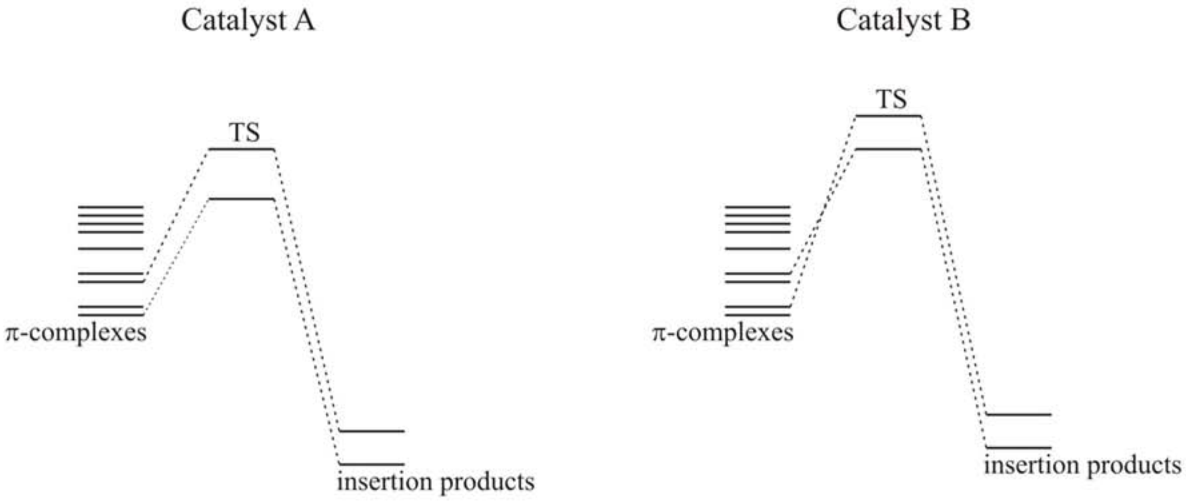
For catalyst A: contribution from alternative propagation pathways *i*

$$k^{A} = \Sigma_i \, \pi_i \, k_i$$

populations π_i , rate constants k_i – based on calculated ΔG

Relative activity of catalysts A and B: k^{A} / k^{B}

Example for two catalysts and two ‚active' insertion pathways



$[\pi^{A}{}_{\text{active1}}]k^{A}{}_{1} + [\pi^{A}{}_{\text{active2}}]k^{A}{}_{2}$

$[\pi^{B}{}_{\text{active1}}]k^{B}{}_{1} + [\pi^{B}{}_{\text{active2}}]k^{B}{}_{2}$

M. Srebro, Ph.D.Thesis 2010

	π-complex	path	ΔG(π)	ΔG(TS)	$\Delta G_a^{\#}$	p_i	k_i	$A_i=p_i \cdot k_i$	$A= \sum A_i \cdot 100$	A_{exp}
R=F	BS	syn	10,54	14,45	3,91	0,1261	0,0086	0,0011	**9,21**	**37,2**
	BS	anti	13,20	16,86	3,66	0,0049	0,0116	0,0001		
	FS	**syn**	**9,21**	**11,00**	**1,79**	**0,6356**	**0,1132**	**0,0719**		
	FS	anti	10,23	12,09	1,87	0,1852	0,1025	0,0190		
R=Cl	BS	syn	10,00	14,12	4,12	0,1469	0,0066	0,0010	**6,85**	**36,0**
	BS	anti	12,98	16,69	3,71	0,0039	0,0109	0,0000		
	FS	**syn**	**8,74**	**10,72**	**1,98**	**0,6793**	**0,0893**	**0,0607**		
	FS	anti	10,08	12,52	2,44	0,1335	0,0509	0,0068		
R=H	BS	syn	10,24	14,99	4,74	0,1441	0,0031	0,0004	**5,12**	**35,2**
	BS	anti	13,25	17,01	3,75	0,0037	0,0103	0,0000		
	FS	**syn**	**9,15**	**11,17**	**2,02**	**0,5478**	**0,0853**	**0,0467**		
	FS	anti	10,41	13,19	2,78	0,1170	0,0339	0,0040		
$R=C(CH_3)_2H$	BS	syn	14,84	18,85	4,01	0,0070	0,0075	0,0001	**5,04**	**34,2**
	BS	anti	14,54	19,91	5,37	0,0100	0,0014	0,0000		
	FS	**syn**	**11,09**	**13,27**	**2,18**	**0,6738**	**0,0699**	**0,0471**		
	FS	anti	11,96	15,45	3,49	0,2315	0,0143	0,0033		
$R=CH_3$	BS	syn	11,42	16,06	4,65	0,0574	0,0069	0,0004	**4,23**	**33,6**
	BS	anti	14,11	17,42	3,31	0,0139	0,0005	0,0000		
	FS	**syn**	**9,81**	**12,22**	**2,40**	**0,5260**	**0,0742**	**0,0390**		
	FS	anti	10,83	14,14	3,31	0,1081	0,0264	0,0029		
$R=C(CH_3)_3$	BS	syn	10,75	14,83	4,08	0,0103	0,0069	0,0001	**3,77**	**33,6**
	BS	anti	11,92	18,23	6,31	0,0125	0,0005	0,0000		
	FS	**syn**	**8,93**	**11,07**	**2,14**	**0,4732**	**0,0742**	**0,0351**		
	FS	anti	10,23	13,21	2,98	0,0972	0,0264	0,0026		
$R=OCH_3$	BS	syn	11,54	13,39	1,85	0,0338	0,1052	0,0036	**1,49**	**22,2**
	BS	anti	14,49	18,79	4,29	0,0009	0,0053	0,0000		
	FS	syn	9,58	13,14	3,55	0,3667	0,0132	0,0048		
	FS	**anti**	**10,54**	**12,89**	**2,35**	**0,1143**	**0,0573**	**0,0066**		

	π-complex	path	$\Delta G(\pi)$	$\Delta G(TS)$	$\Delta G_a^\#$	A_{exp}
R=F	BS	syn	10,54	14,45	3,91	**37,2**
	BS	anti	13,20	16,86	3,66	
	FS	**syn**	**9,21**	**11,00**	**1,79**	
	FS	anti	10,23	12,09	1,87	
R=Cl	BS	syn	10,00	14,12	4,12	**36,0**
	BS	anti	12,98	16,69	3,71	
	FS	**syn**	**8,74**	**10,72**	**1,98**	
	FS	anti	10,08	12,52	2,44	
R=H	BS	syn	10,24	14,99	4,74	**35,2**
	BS	anti	13,25	17,01	3,75	
	FS	**syn**	**9,15**	**11,17**	**2,02**	
	FS	anti	10,41	13,19	2,78	
R=C(CH_3)$_2$H	BS	syn	14,84	18,85	4,01	**34,2**
	BS	anti	14,54	19,91	5,37	
	FS	**syn**	**11,09**	**13,27**	**2,18**	
	FS	anti	11,96	15,45	3,49	
R=CH_3	BS	syn	11,42	16,06	4,65	**33,6**
	BS	anti	14,11	17,42	3,31	
	FS	**syn**	**9,81**	**12,22**	**2,40**	
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	BS	anti	11,92	18,23	6,31	
	FS	**syn**	**8,93**	**11,07**	**2,14**	
	FS	anti	10,23	13,21	2,98	
R=OCH_3	BS	syn	11,54	13,39	1,85	**22,2**
	BS	anti	14,49	18,79	4,29	
	FS	syn	9,58	13,14	3,55	
	FS	**anti**	**10,54**	**12,89**	**2,35**	

	π-complex	path	ΔG(π)	ΔG(TS)	$\Delta G_a^{\#}$	p_i	A_{exp}
R=F	BS	syn	10,54	14,45	3,91	0,1261	**37,2**
	BS	anti	13,20	16,86	3,66	0,0049	
	FS	**syn**	**9,21**	**11,00**	**1,79**	**0,6356**	
	FS	anti	10,23	12,09	1,87	0,1852	
R=Cl	BS	syn	10,00	14,12	4,12	0,1469	**36,0**
	BS	anti	12,98	16,69	3,71	0,0039	
	FS	**syn**	**8,74**	**10,72**	**1,98**	**0,6793**	
	FS	anti	10,08	12,52	2,44	0,1335	
R=H	BS	syn	10,24	14,99	4,74	0,1441	**35,2**
	BS	anti	13,25	17,01	3,75	0,0037	
	FS	**syn**	**9,15**	**11,17**	**2,02**	**0,5478**	
	FS	anti	10,41	13,19	2,78	0,1170	
R=C(CH$_3$)$_2$H	BS	syn	14,84	18,85	4,01	0,0070	**34,2**
	BS	anti	14,54	19,91	5,37	0,0100	
	FS	**syn**	**11,09**	**13,27**	**2,18**	**0,6738**	
	FS	anti	11,96	15,45	3,49	0,2315	
R=CH$_3$	BS	syn	11,42	16,06	4,65	0,0574	**33,6**
	BS	anti	14,11	17,42	3,31	0,0139	
	FS	**syn**	**9,81**	**12,22**	**2,40**	**0,5260**	
	FS	anti	10,83	14,14	3,31	0,1081	
R=C(CH$_3$)$_3$	BS	syn	10,75	14,83	4,08	0,0103	**33,6**
	BS	anti	11,92	18,23	6,31	0,0125	
	FS	**syn**	**8,93**	**11,07**	**2,14**	**0,4732**	
	FS	anti	10,23	13,21	2,98	0,0972	
R=OCH$_3$	BS	syn	11,54	13,39	1,85	0,0338	**22,2**
	BS	anti	14,49	18,79	4,29	0,0009	
	FS	syn	9,58	13,14	3,55	0,3667	
	FS	**anti**	**10,54**	**12,89**	**2,35**	**0,1143**	

	π-complex	path	ΔG(π)	ΔG(TS)	$\Delta G_a^{\#}$	p_i	k_i	A_{exp}
R=F	BS	syn	10,54	14,45	3,91	0,1261	0,0086	**37,2**
	BS	anti	13,20	16,86	3,66	0,0049	0,0116	
	FS	**syn**	**9,21**	**11,00**	**1,79**	**0,6356**	**0,1132**	
	FS	anti	10,23	12,09	1,87	0,1852	0,1025	
R=Cl	BS	syn	10,00	14,12	4,12	0,1469	0,0066	**36,0**
	BS	anti	12,98	16,69	3,71	0,0039	0,0109	
	FS	**syn**	**8,74**	**10,72**	**1,98**	**0,6793**	**0,0893**	
	FS	anti	10,08	12,52	2,44	0,1335	0,0509	
R=H	BS	syn	10,24	14,99	4,74	0,1441	0,0031	**35,2**
	BS	anti	13,25	17,01	3,75	0,0037	0,0103	
	FS	**syn**	**9,15**	**11,17**	**2,02**	**0,5478**	**0,0853**	
	FS	anti	10,41	13,19	2,78	0,1170	0,0339	
R=C(CH$_3$)$_2$H	BS	syn	14,84	18,85	4,01	0,0070	0,0075	**34,2**
	BS	anti	14,54	19,91	5,37	0,0100	0,0014	
	FS	**syn**	**11,09**	**13,27**	**2,18**	**0,6738**	**0,0699**	
	FS	anti	11,96	15,45	3,49	0,2315	0,0143	
R=CH$_3$	BS	syn	11,42	16,06	4,65	0,0574	0,0069	**33,6**
	BS	anti	14,11	17,42	3,31	0,0139	0,0005	
	FS	**syn**	**9,81**	**12,22**	**2,40**	**0,5260**	**0,0742**	
	FS	anti	10,83	14,14	3,31	0,1081	0,0264	
R=C(CH$_3$)$_3$	BS	syn	10,75	14,83	4,08	0,0103	0,0069	**33,6**
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	FS	**syn**	**8,93**	**11,07**	**2,14**	**0,4732**	**0,0742**	
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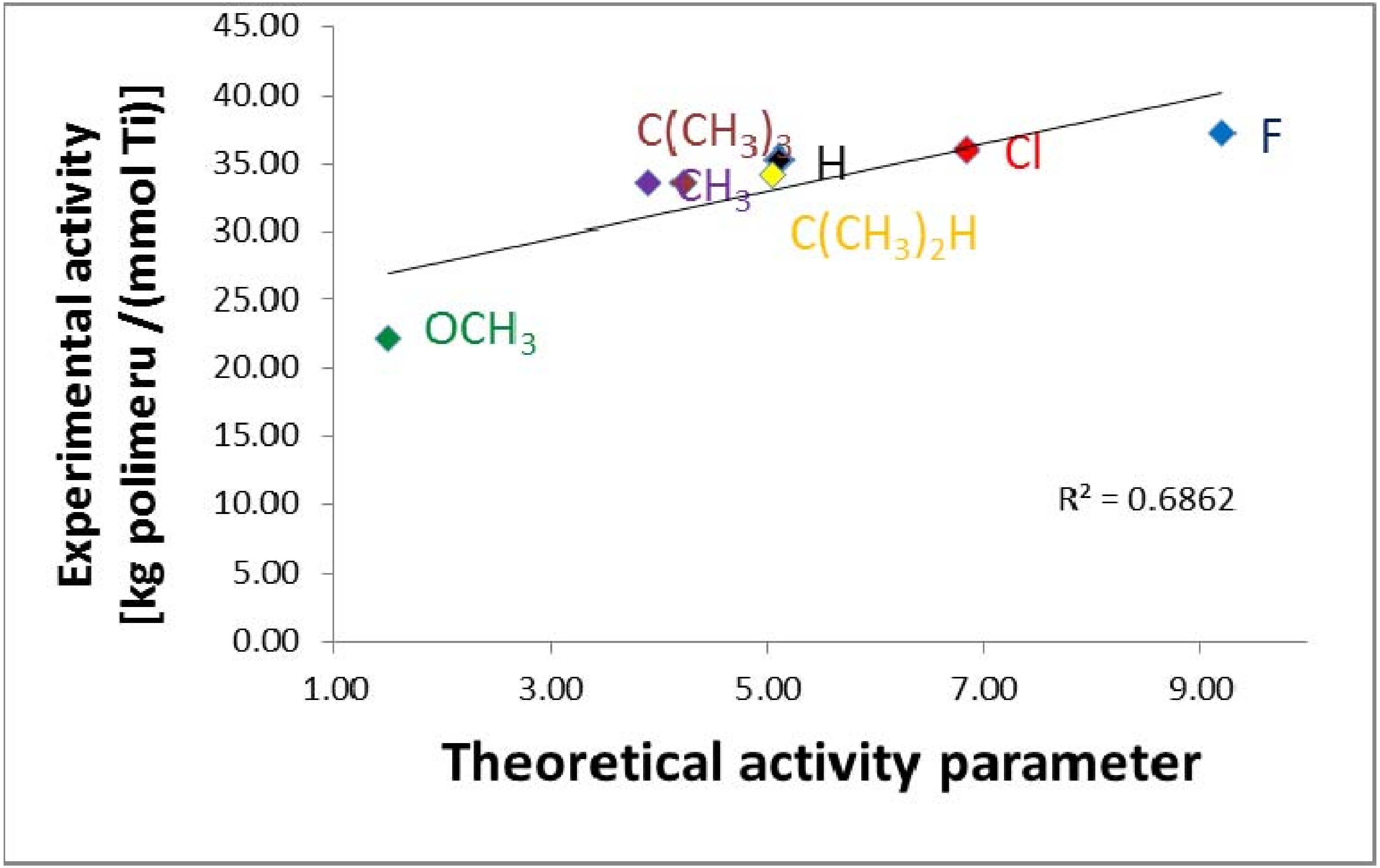
	BS	anti	14,49	18,79	4,29	0,0009	0,0053	
	FS	syn	9,58	13,14	3,55	0,3667	0,0132	
	FS	**anti**	**10,54**	**12,89**	**2,35**	**0,1143**	**0,0573**	

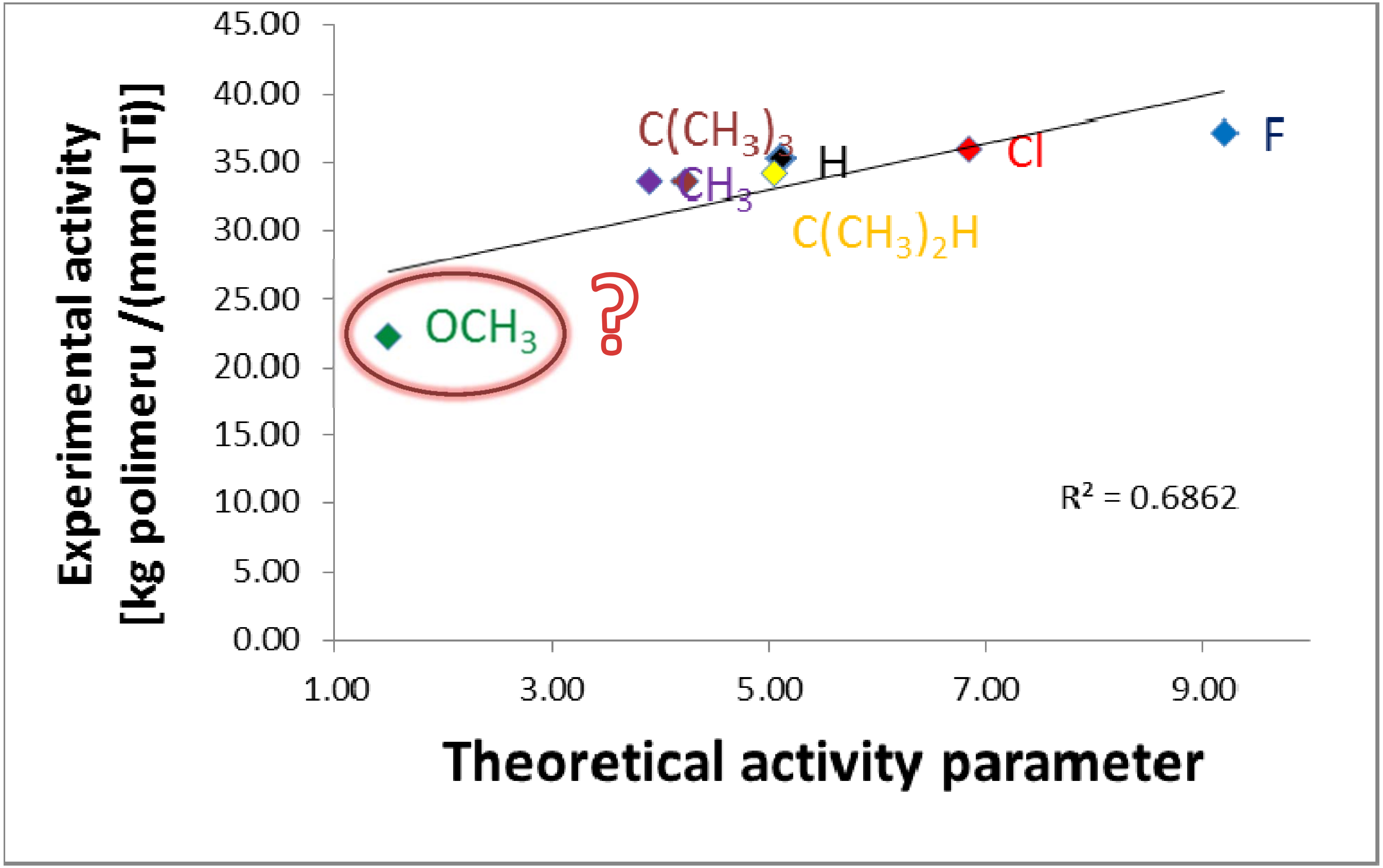
	π-complex	path	$\Delta G(\pi)$	$\Delta G(TS)$	$\Delta G_a^{\#}$	p_i	k_i	$A_i=p_i\cdot k_i$	A_{exp}
R=F	BS	syn	10,54	14,45	3,91	0,1261	0,0086	0,0011	**37,2**
	BS	anti	13,20	16,86	3,66	0,0049	0,0116	0,0001	
	FS	**syn**	**9,21**	**11,00**	**1,79**	**0,6356**	**0,1132**	**0,0719**	
	FS	anti	10,23	12,09	1,87	0,1852	0,1025	0,0190	
R=Cl	BS	syn	10,00	14,12	4,12	0,1469	0,0066	0,0010	**36,0**
	BS	anti	12,98	16,69	3,71	0,0039	0,0109	0,0000	
	FS	**syn**	**8,74**	**10,72**	**1,98**	**0,6793**	**0,0893**	**0,0607**	
	FS	anti	10,08	12,52	2,44	0,1335	0,0509	0,0068	
R=H	BS	syn	10,24	14,99	4,74	0,1441	0,0031	0,0004	**35,2**
	BS	anti	13,25	17,01	3,75	0,0037	0,0103	0,0000	
	FS	**syn**	**9,15**	**11,17**	**2,02**	**0,5478**	**0,0853**	**0,0467**	
	FS	anti	10,41	13,19	2,78	0,1170	0,0339	0,0040	
R=C(CH$_3$)$_2$H	BS	syn	14,84	18,85	4,01	0,0070	0,0075	0,0001	**34,2**
	BS	anti	14,54	19,91	5,37	0,0100	0,0014	0,0000	
	FS	**syn**	**11,09**	**13,27**	**2,18**	**0,6738**	**0,0699**	**0,0471**	
	FS	anti	11,96	15,45	3,49	0,2315	0,0143	0,0033	
R=CH$_3$	BS	syn	11,42	16,06	4,65	0,0574	0,0069	0,0004	**33,6**
	BS	anti	14,11	17,42	3,31	0,0139	0,0005	0,0000	
	FS	**syn**	**9,81**	**12,22**	**2,40**	**0,5260**	**0,0742**	**0,0390**	
	FS	anti	10,83	14,14	3,31	0,1081	0,0264	0,0029	
R=C(CH$_3$)$_3$	BS	syn	10,75	14,83	4,08	0,0103	0,0069	0,0001	**33,6**
	BS	anti	11,92	18,23	6,31	0,0125	0,0005	0,0000	
	FS	**syn**	**8,93**	**11,07**	**2,14**	**0,4732**	**0,0742**	**0,0351**	
	FS	anti	10,23	13,21	2,98	0,0972	0,0264	0,0026	
R=OCH$_3$	BS	syn	11,54	13,39	1,85	0,0338	0,1052	0,0036	**22,2**
	BS	anti	14,49	18,79	4,29	0,0009	0,0053	0,0000	
	FS	syn	9,58	13,14	3,55	0,3667	0,0132	0,0048	
	FS	**anti**	**10,54**	**12,89**	**2,35**	**0,1143**	**0,0573**	**0,0066**	

	π-complex	path	ΔG(π)	ΔG(TS)	$\Delta G_a^{\#}$	p_i	k_i	$A_i=p_i \cdot k_i$	$A= \sum A_i \cdot 100$	A_{exp}
R=F	BS	syn	10,54	14,45	3,91	0,1261	0,0086	0,0011	**9,21**	**37,2**
	BS	anti	13,20	16,86	3,66	0,0049	0,0116	0,0001		
	FS	**syn**	**9,21**	**11,00**	**1,79**	**0,6356**	**0,1132**	**0,0719**		
	FS	anti	10,23	12,09	1,87	0,1852	0,1025	0,0190		
R=Cl	BS	syn	10,00	14,12	4,12	0,1469	0,0066	0,0010	**6,85**	**36,0**
	BS	anti	12,98	16,69	3,71	0,0039	0,0109	0,0000		
	FS	**syn**	**8,74**	**10,72**	**1,98**	**0,6793**	**0,0893**	**0,0607**		
	FS	anti	10,08	12,52	2,44	0,1335	0,0509	0,0068		
R=H	BS	syn	10,24	14,99	4,74	0,1441	0,0031	0,0004	**5,12**	**35,2**
	BS	anti	13,25	17,01	3,75	0,0037	0,0103	0,0000		
	FS	**syn**	**9,15**	**11,17**	**2,02**	**0,5478**	**0,0853**	**0,0467**		
	FS	anti	10,41	13,19	2,78	0,1170	0,0339	0,0040		
R=C(CH$_3$)$_2$H	BS	syn	14,84	18,85	4,01	0,0070	0,0075	0,0001	**5,04**	**34,2**
	BS	anti	14,54	19,91	5,37	0,0100	0,0014	0,0000		
	FS	**syn**	**11,09**	**13,27**	**2,18**	**0,6738**	**0,0699**	**0,0471**		
	FS	anti	11,96	15,45	3,49	0,2315	0,0143	0,0033		
R=CH$_3$	BS	syn	11,42	16,06	4,65	0,0574	0,0069	0,0004	**4,23**	**33,6**
	BS	anti	14,11	17,42	3,31	0,0139	0,0005	0,0000		
	FS	**syn**	**9,81**	**12,22**	**2,40**	**0,5260**	**0,0742**	**0,0390**		
	FS	anti	10,83	14,14	3,31	0,1081	0,0264	0,0029		
R=C(CH$_3$)$_3$	BS	syn	10,75	14,83	4,08	0,0103	0,0069	0,0001	**3,77**	**33,6**
	BS	anti	11,92	18,23	6,31	0,0125	0,0005	0,0000		
	FS	**syn**	**8,93**	**11,07**	**2,14**	**0,4732**	**0,0742**	**0,0351**		
	FS	anti	10,23	13,21	2,98	0,0972	0,0264	0,0026		
R=OCH$_3$	BS	syn	11,54	13,39	1,85	0,0338	0,1052	0,0036	**1,49**	**22,2**
	BS	anti	14,49	18,79	4,29	0,0009	0,0053	0,0000		
	FS	syn	9,58	13,14	3,55	0,3667	0,0132	0,0048		
	FS	**anti**	**10,54**	**12,89**	**2,35**	**0,1143**	**0,0573**	**0,0066**		

Theoretical vs experimental activity



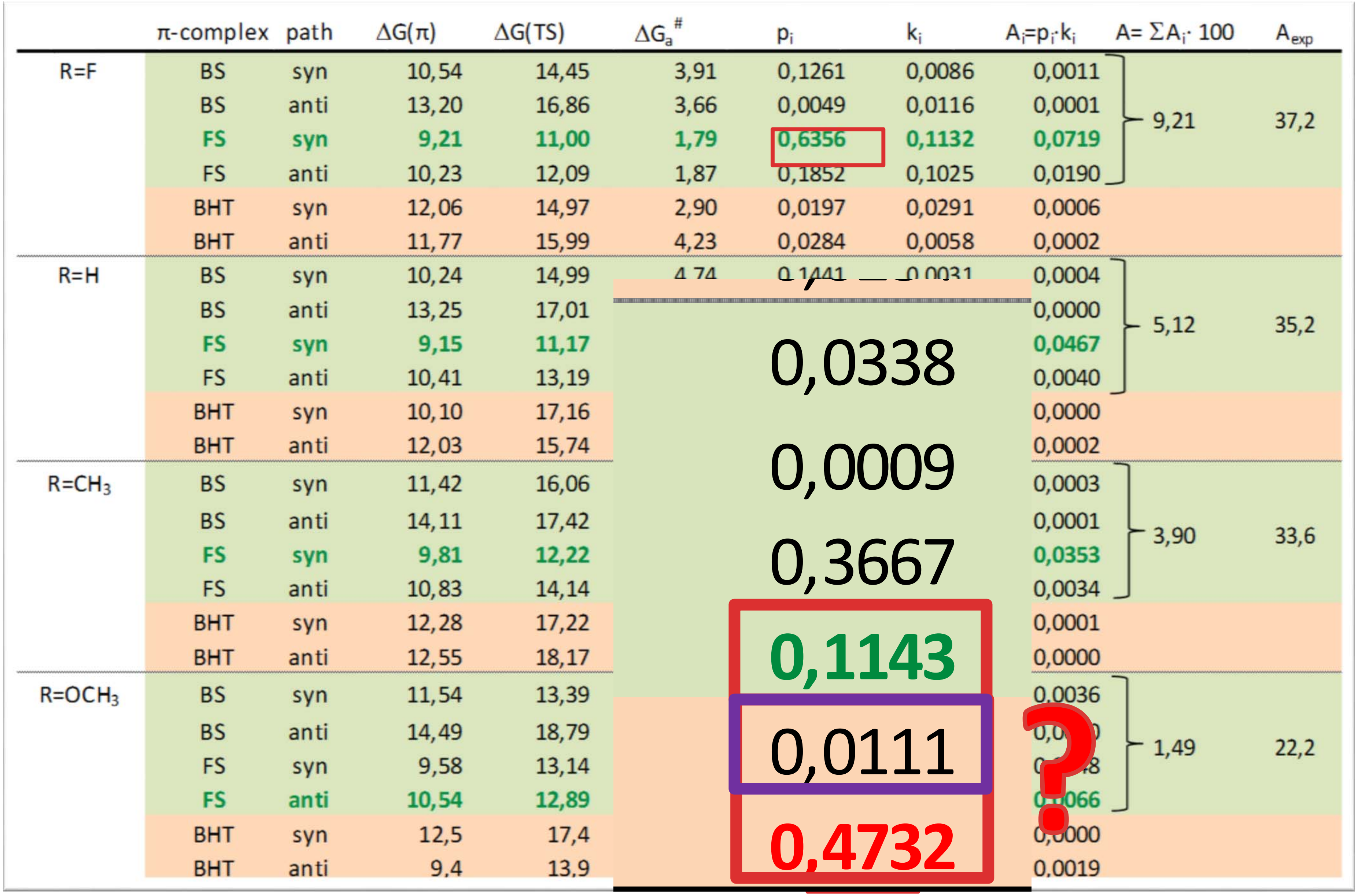
Theoretical vs experimental activity



Populations of pathways

	π-complex	path	ΔG(π)	ΔG(TS)	$\Delta G_a^{\#}$	p_i	k_i	$A_i = p_i \cdot k_i$	$A = \Sigma A_i \cdot 100$	A_{exp}
R=F	BS	syn	10,54	14,45	3,91	0,1261	0,0086	0,0011	9,21	37,2
	BS	anti	13,20	16,86	3,66	0,0049	0,0116	0,0001		
	FS	**syn**	**9,21**	**11,00**	**1,79**	**0,6356**	**0,1132**	**0,0719**		
	FS	anti	10,23	12,09	1,87	0,1852	0,1025	0,0190		
	BHT	syn	12,06	14,97	2,90	0,0197	0,0291	0,0006		
	BHT	anti	11,77	15,99	4,23	0,0284	0,0058	0,0002		
R=H	BS	syn	10,24	14,99	4,74	0,1441	0,0031	0,0004	5,12	35,2
	BS	anti	13,25	17,01	3,75	0,0037	0,0103	0,0000		
	FS	**syn**	**9,15**	**11,17**	**2,02**	**0,5478**	**0,0853**	**0,0467**		
	FS	anti	10,41	13,19	2,78	0,1170	0,0339	0,0040		
	BHT	syn	10,10	17,16	7,06	0,1711	0,0002	0,0000		
	BHT	anti	12,03	15,74	3,72	0,0164	0,0108	0,0002		
R=CH_3	BS	syn	11,42	16,06	4,65	0,0931	0,0035	0,0003	3,90	33,6
	BS	anti	14,11	17,42	3,31	0,0035	0,0177	0,0001		
	FS	**syn**	**9,81**	**12,22**	**2,40**	**0,6577**	**0,0536**	**0,0353**		
	FS	anti	10,83	14,14	3,31	0,1898	0,0177	0,0034		
	BHT	syn	12,28	17,22	4,94	0,0325	0,0024	0,0001		
	BHT	anti	12,55	18,17	5,62	0,0234	0,0011	0,0000		
R=OCH_3	BS	syn	11,54	13,39	1,85	0,0338	0,1052	0,0036	1,49	22,2
	BS	anti	14,49	18,79	4,29	0,0009	0,0053 ?	0,0000		
	FS	syn	9,58	13,14	3,55	0,3667	0,0132	0,0048		
	FS	**anti**	**10,54**	**12,89**	**2,35**	**0,1143**	**0,0573**	**0,0066**		
	BHT	syn	12,5	17,4	4,9	0,0111	0,0025	0,0000		
	BHT	anti	9,4	13,9	4,5	**0,4732**	0,0040	0,0019		

Populations of pathways



	π-complex	path	ΔG(π)	ΔG(TS)	$\Delta G_a^{\#}$	p_i	k_i	$A_i=p_i \cdot k_i$	$A= \Sigma A_i \cdot 100$	A_{exp}
R=F	BS	syn	10,54	14,45	3,91	0,1261	0,0086	0,0011	9,21	37,2
	BS	anti	13,20	16,86	3,66	0,0049	0,0116	0,0001		
	FS	**syn**	**9,21**	**11,00**	**1,79**	**0,6356**	**0,1132**	**0,0719**		
	FS	anti	10,23	12,09	1,87	0,1852	0,1025	0,0190		
	BHT	syn	12,06	14,97	2,90	0,0197	0,0291	0,0006		
	BHT	anti	11,77	15,99	4,23	0,0284	0,0058	0,0002		
R=H	BS	syn	10,24	14,99	4,74	0,1441	0,0031	0,0004	5,12	35,2
	BS	anti	13,25	17,01	[illegible]	[illegible]	[illegible]	0,0000		
	FS	**syn**	**9,15**	**11,17**	[illegible]	[illegible]	[illegible]	**0,0467**		
	FS	anti	10,41	13,19	[illegible]	[illegible]	[illegible]	0,0040		
	BHT	syn	10,10	17,16	[illegible]	[illegible]	[illegible]	0,0000		
	BHT	anti	12,03	15,74	[illegible]	[illegible]	[illegible]	0,0002		
R=CH_3	BS	syn	11,42	16,06	[illegible]	[illegible]	[illegible]	0,0003	3,90	33,6
	BS	anti	14,11	17,42	[illegible]	[illegible]	[illegible]	0,0001		
	FS	**syn**	**9,81**	**12,22**	[illegible]	[illegible]	[illegible]	**0,0353**		
	FS	anti	10,83	14,14	[illegible]	[illegible]	[illegible]	0,0034		
	BHT	syn	12,28	17,22	[illegible]	[illegible]	[illegible]	0,0001		
	BHT	anti	12,55	18,17	[illegible]	[illegible]	[illegible]	0,0000		
R=OCH_3	BS	syn	11,54	13,39	[illegible]	[illegible]	[illegible]	0,0036	1,49	22,2
	BS	anti	14,49	18,79	[illegible]	[illegible]	[illegible]	[illegible]		
	FS	syn	9,58	13,14	[illegible]	[illegible]	[illegible]	[illegible]		
	FS	**anti**	**10,54**	**12,89**	[illegible]	[illegible]	[illegible]	**0,0066**		
	BHT	syn	12,5	17,4	[illegible]	[illegible]	[illegible]	0,0000		
	BHT	anti	9,4	13,9	[illegible]	[illegible]	[illegible]	0,0019		

0,0338

0,0009

0,3667

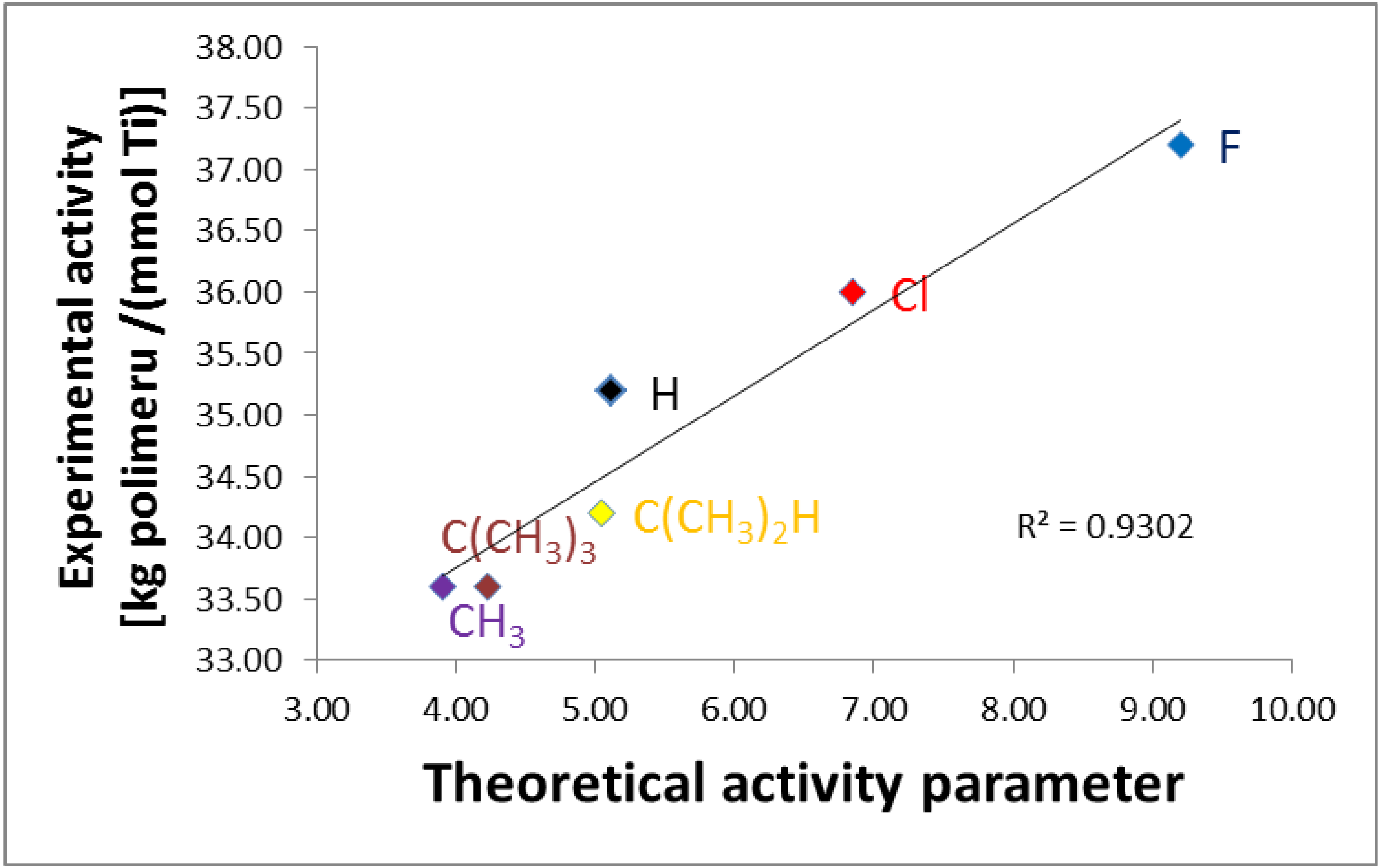
0,1143

0,0111

0,4732

?

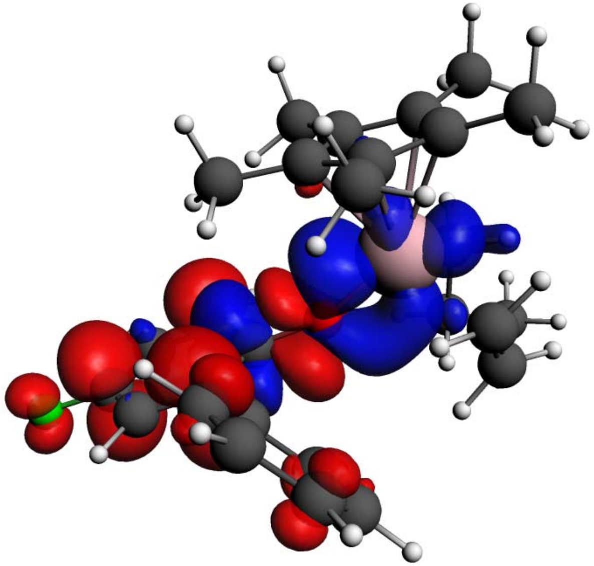
Theoretical vs experimental activity



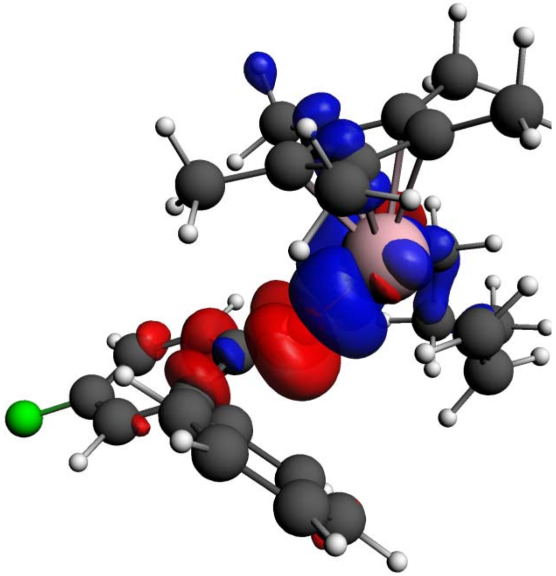
	π-complex	path	ΔE_{Pauli}	ΔE_{elstat}	ΔE_{steric}	ΔE_{orb}	$\Delta E_{bonding}$	$A_i=p_i\cdot k_i$
R=F	BS	syn	122,87	-245,72	-122,85	-148,40	-271,25	0,0011
	BS	anti	123,38	-243,55	-120,17	-148,07	-268,24	0,0001
	FS	**syn**	120,61	-244,18	**-123,57**	-149,00	**-272,57**	**0,0719**
	FS	anti	119,95	-241,21	-121,26	-151,04	-272,30	0,0190
R=Cl	BS	syn	121,73	-241,31	-119,58	-147,76	-267,34	0,0010
	BS	anti	122,51	-239,40	-116,89	-147,59	-264,48	0,0000
	FS	**syn**	119,36	-239,92	**-120,56**	-148,11	**-268,67**	**0,0607**
	FS	anti	118,84	-236,90	-118,06	-150,25	-268,31	0,0068
R=H	BS	syn	123,30	-248,99	-125,69	-149,24	-274,92	0,0004
	BS	anti	124,58	-247,14	-122,56	-149,08	-271,64	0,0000
	FS	**syn**	121,23	-247,85	**-126,62**	-149,45	**-276,06**	**0,0467**
	FS	anti	121,08	-244,71	-123,63	-151,79	-275,43	0,0040
R=C(CH$_3$)$_2$H	BS	syn	124,98	-247,29	**-122,31**	-154,17	-276,48	0,0001
	BS	anti	126,45	-245,57	-119,12	-154,08	-273,20	0,0000
	FS	**syn**	122,98	-245,28	**-122,30**	-155,77	**-278,07**	**0,0471**
	FS	anti	122,37	-243,52	-121,15	-156,98	-278,13	0,0033
R=CH$_3$	BS	syn	124,73	-249,07	-124,34	-152,52	-276,86	0,0003
	BS	anti	125,97	-246,78	-120,81	-152,49	-273,29	0,0001
	FS	**syn**	122,52	-247,47	**-124,95**	-153,64	**-278,58**	**0,0353**
	FS	anti	121,85	-244,81	-122,96	-155,29	-278,25	0,0034
R=C(CH$_3$)$_3$	BS	syn	125,31	-247,69	**-122,38**	-155,01	-277,38	0,0001
	BS	anti	126,80	-245,63	-118,83	-154,83	-273,66	0,0000
	FS	**syn**	123,11	-245,41	**-122,30**	-156,15	**-278,44**	**0,0351**
	FS	anti	122,66	-243,28	-120,62	-157,53	-278,15	0,0026
R=OCH$_3$	BS	syn	125,73	-251,26	-125,53	-155,40	-280,92	0,0036
	BS	anti	126,46	-248,96	-122,50	-154,99	-277,49	0,0000
	FS	**syn**	123,00	-248,75	**-125,75**	-156,95	-282,70	0,0048
	FS	anti	121,66	-246,44	-124,78	-158,18	**-282,95**	**0,0066**

	π-complex	path	ΔE_{Pauli}	ΔE_{elstat}	ΔE_{steric}	ΔE_{orb}	$\Delta E_{bonding}$	$A_i=p_i\cdot k_i$
R=F	BS	syn					-271,25	0,0011
	BS	anti					-268,24	0,0001
	FS	**syn**				**FS_syn**	**-272,57**	**0,0719**
	FS	anti					-272,30	0,0190
R=Cl	BS	syn					-267,34	0,0010
	BS	anti					-264,48	0,0000
	FS	**syn**				**FS_syn**	**-268,67**	**0,0607**
	FS	anti					-268,31	0,0068
R=H	BS	syn					-274,92	0,0004
	BS	anti					-271,64	0,0000
	FS	**syn**				**FS_syn**	**-276,06**	**0,0467**
	FS	anti					-275,43	0,0040
$R=C(CH_3)_2H$	BS	syn					-276,48	0,0001
	BS	anti					-273,20	0,0000
	FS	**syn**				**FS_syn**	**-278,07**	**0,0471**
	FS	anti					-278,13	0,0033
$R=CH_3$	BS	syn					-276,86	0,0003
	BS	anti					-273,29	0,0001
	FS	**syn**				**FS_syn**	**-278,58**	**0,0353**
	FS	anti					-278,25	0,0034
$R=C(CH_3)_3$	BS	syn					-277,38	0,0001
	BS	anti					-273,66	0,0000
	FS	**syn**				**FS_syn**	**-278,44**	**0,0351**
	FS	anti					-278,15	0,0026
$R=OCH_3$	BS	syn					-280,92	0,0036
	BS	anti					-277,49	0,0000
	FS	**syn**					-282,70	0,0048
	FS	anti				**FS_anti**	**-282,95**	**0,0066**

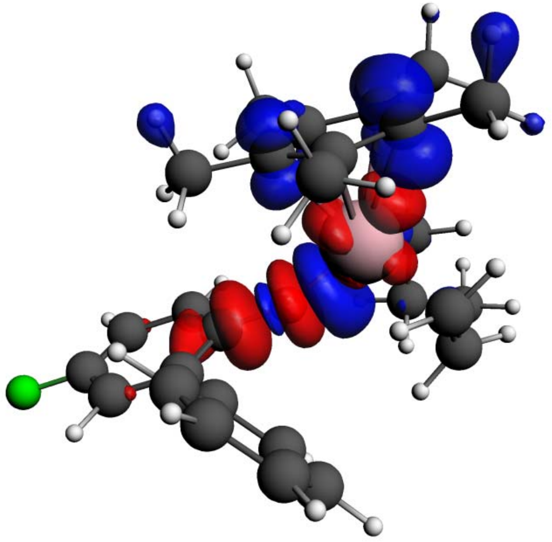
Orbital interaction in precatalyst.



ΔE^{1}_{orb}=-53.53kcal/mol



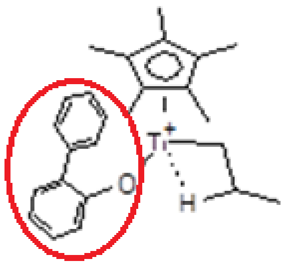
ΔE^{2}_{orb}=-28.32kcal/mol



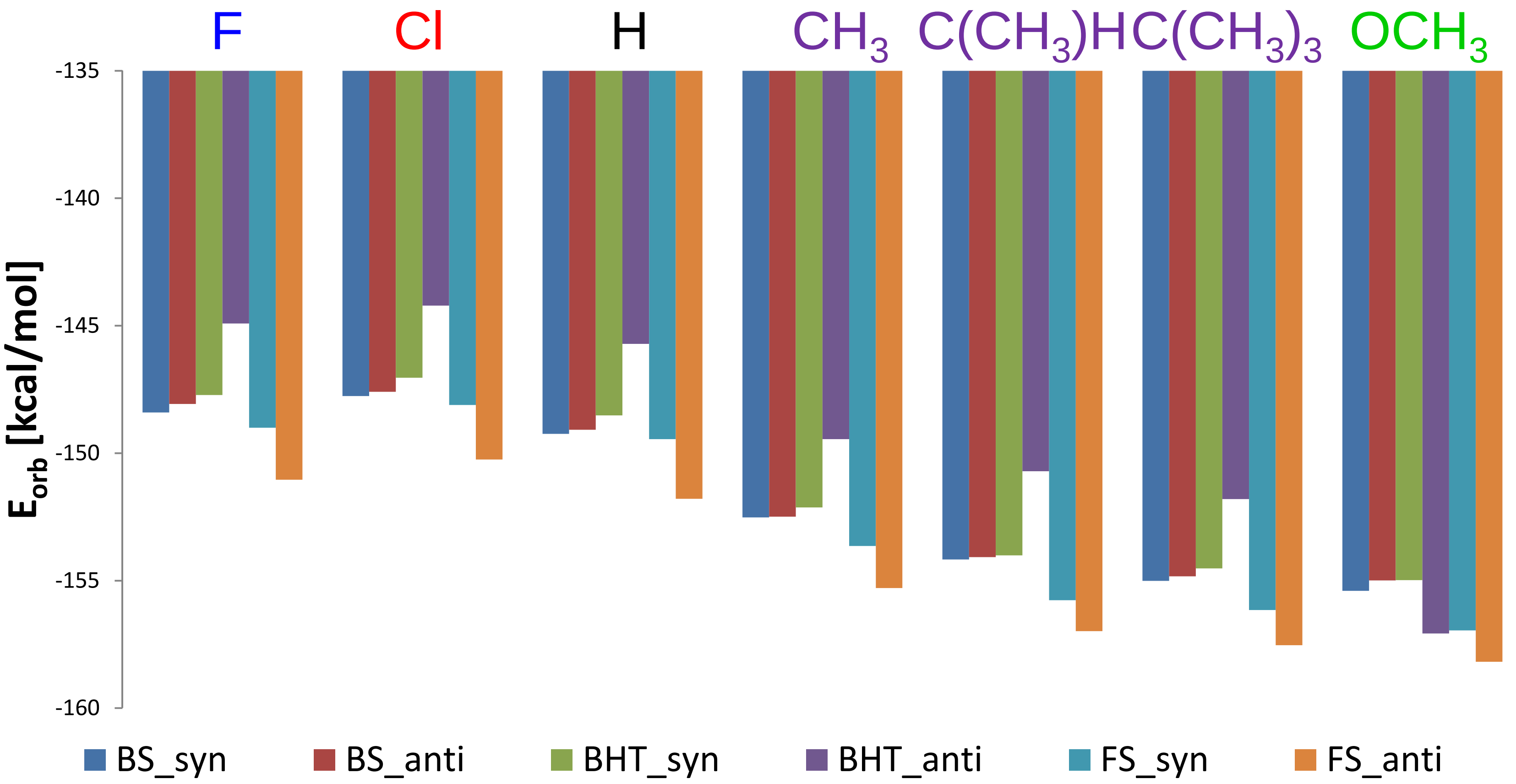
ΔE^{3}_{orb}=-29.55kcal/mol

The ETS-NOCV dominating contribution to the deformational density, Δρ, according to the ETS-NOCV analysis for the interaction of Ti-O bond.

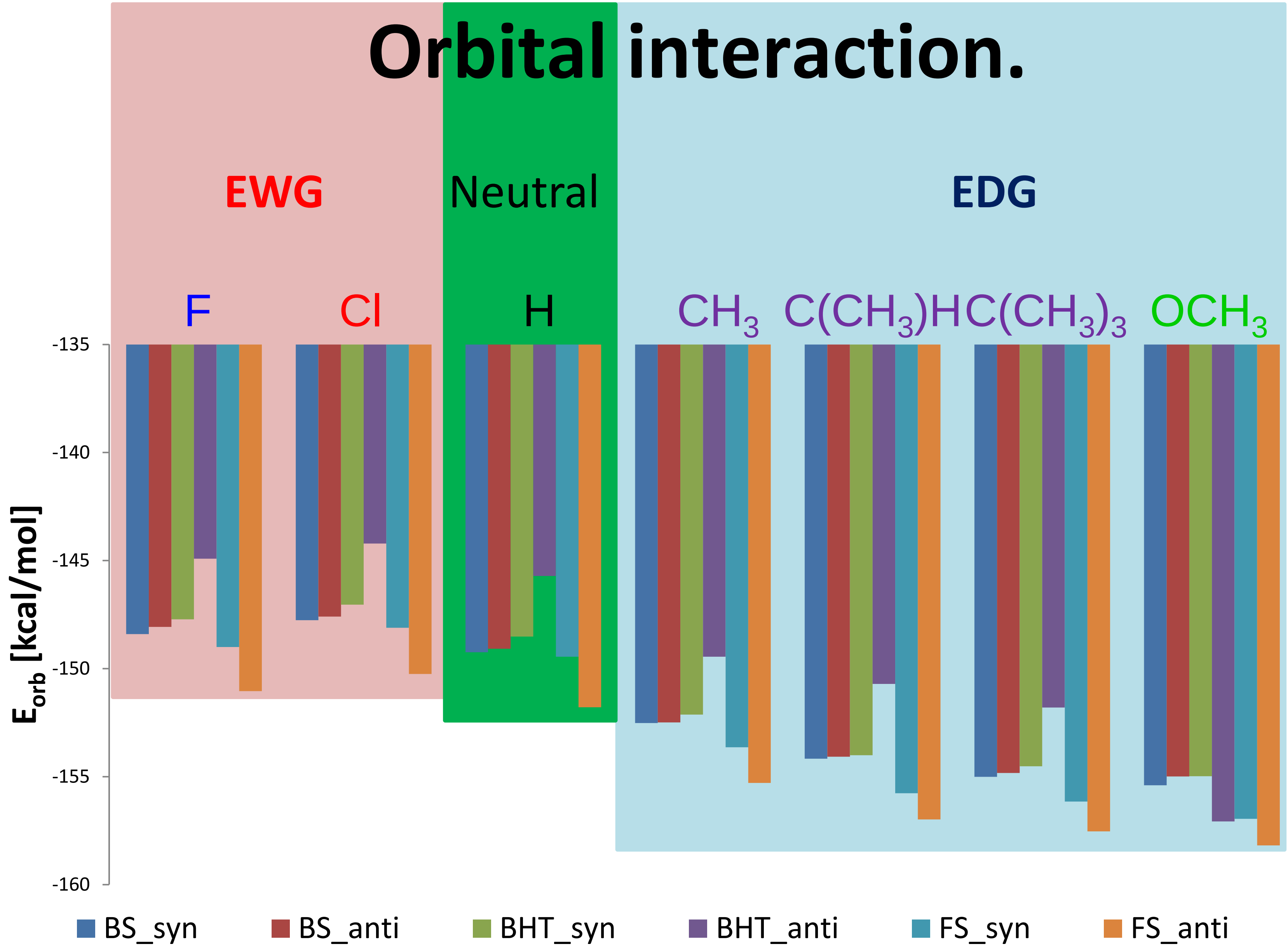
The fragment selection:



Orbital interaction.



Orbital interaction.



Main Conclusions

- Theoretical activity parameter, based on both, the activation barriers and the π-complex populations, correlates well with experimental activity.
- The nature of electron withdrawing and donating groups was characterized by ETS-NOCV methodology.
- The substituents on the ligand affect the charge on Ti and the strenght of Ti-O bonding (electron push-pull effect); the changes in the orbital interaction term are mostly responsible for the substituent effect on the total bonding energy.

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Orbital interaction in precatalyst.