Data Handling and Informatics Tools for Model-Based Discovery

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with

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and

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Chemical Engineering, Chemistry, Computer Graphics Technology, Computer Science, Electrical & Computer Engineering, Industrial Engineering, ITaP, Cyber Center, Envision Center and Center for Catalyst Design

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ExxonMobil
Cummins
Equistar Chemicals
Purdue University

Current Data Archiving Methods

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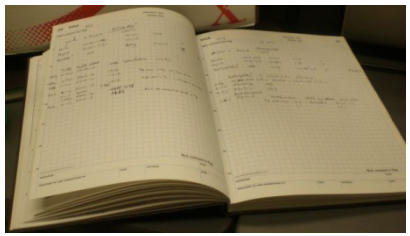
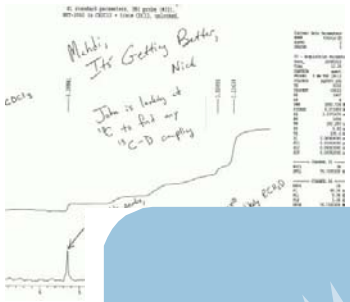
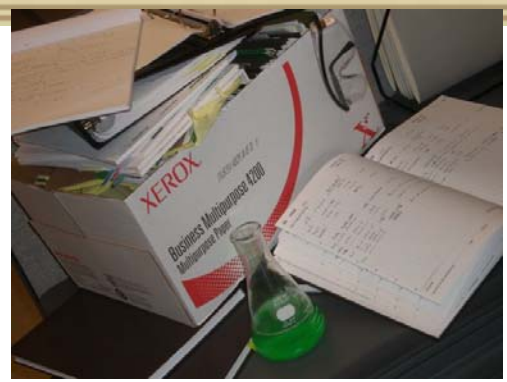




At the end of



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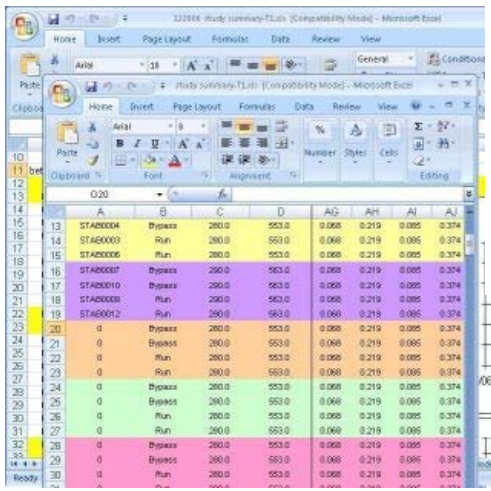
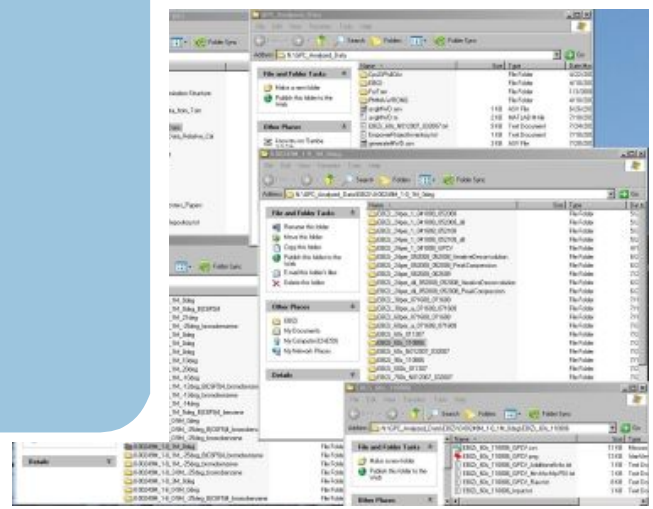
Metadata i





Stored in Windows nested file folders
Can not be searched

Current situation is barely manageable, but just think about scaling-up with high throughput data

1st Group + 2nd Group . . . + . . nth Group



x10 **x10** **x10**

- How we can one integrate data from different groups?
- How does one ensure data persistence?
- How does one assign intellectual ownership of group data?
- How can this be done for a small research effort like the battery community?

CyberInfrastructure for Chemical Research

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- ***How can CyberInfrastructure aid in the extraction of useful knowledge from the flood of data ?***
- ***Requirements***
  - ***Single time of ingress***
  - ***Databases, not folders, that are ontologically enabled***
    (i.e. can be searched with words/concepts that have chemical meaning)
  - ***Analysis programs integrate with database***
  - ***Advanced visualization tools for human processing of information***
  - ***Must be low friction - the researcher can focus on chemistry not IT tools***

SciAether™

Science: *the process of systematically generating knowledge from data*

Aether: *the magical substance postulated by the late 19th century physicists that supported all physical processes*

Outline

- *Data Ingress – e-Lab Notebook*
- *Database – ontologically enabled*
- *Integrated analysis environment*
- *Analysis tools*
- *Visualization*
- *Computer-aided discovery*

Requirements of e-Lab Notebook

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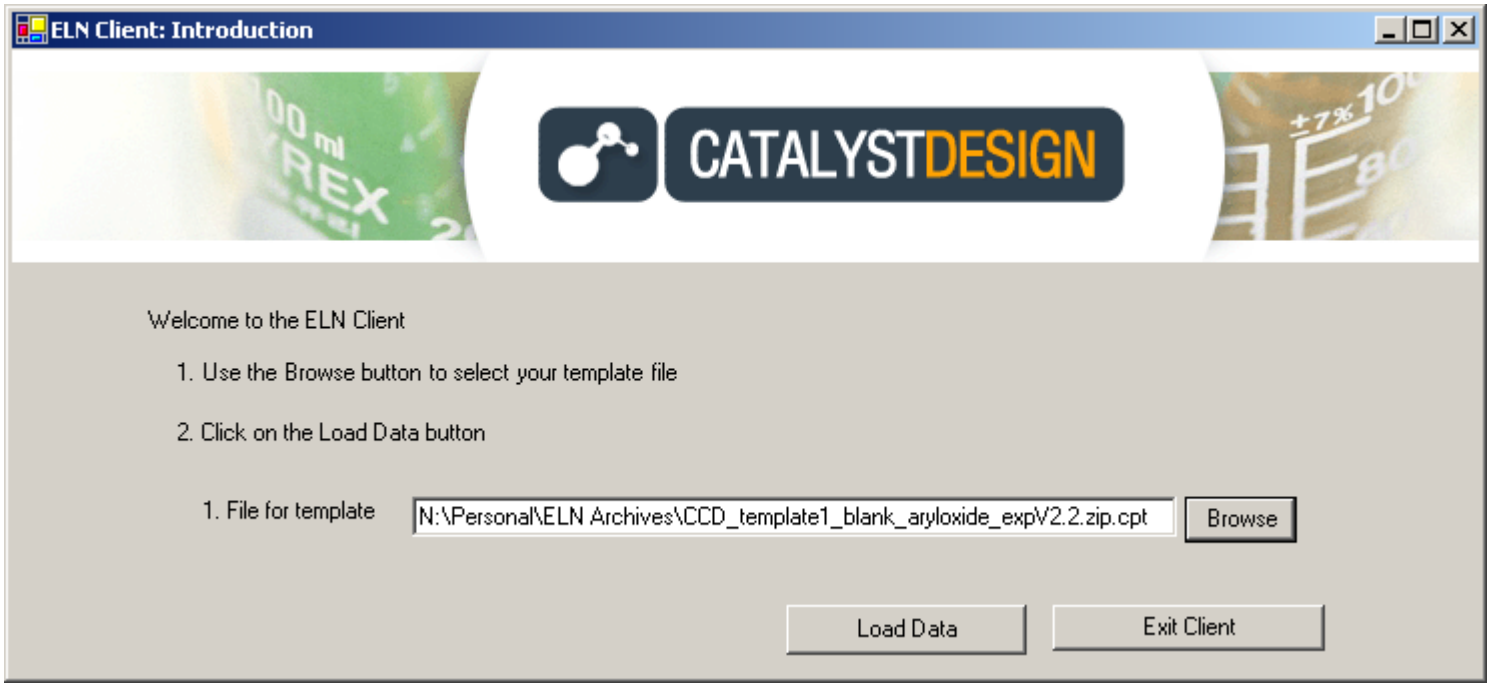
1. **Intuitive interface that creates connections in the database**
2. **Ability to easily create new templates**
3. **eLN has to be able to work offline**
4. **Interface should allow integration with 3rd party software (e.g. Chemsketch, etc.)**
5. **Ability to attach raw/binary data from instruments**
6. **Interface should have ability to enter symbols and equations**
7. **The e-Lab Notebook should freeze all data at the end of the day and time stamp the data – legal IP protocol**
8. **Data provenance must be archived**

Data must only be ingressed a single time – no copying from paper notebook

e-Lab Notebook



e-Lab Notebook

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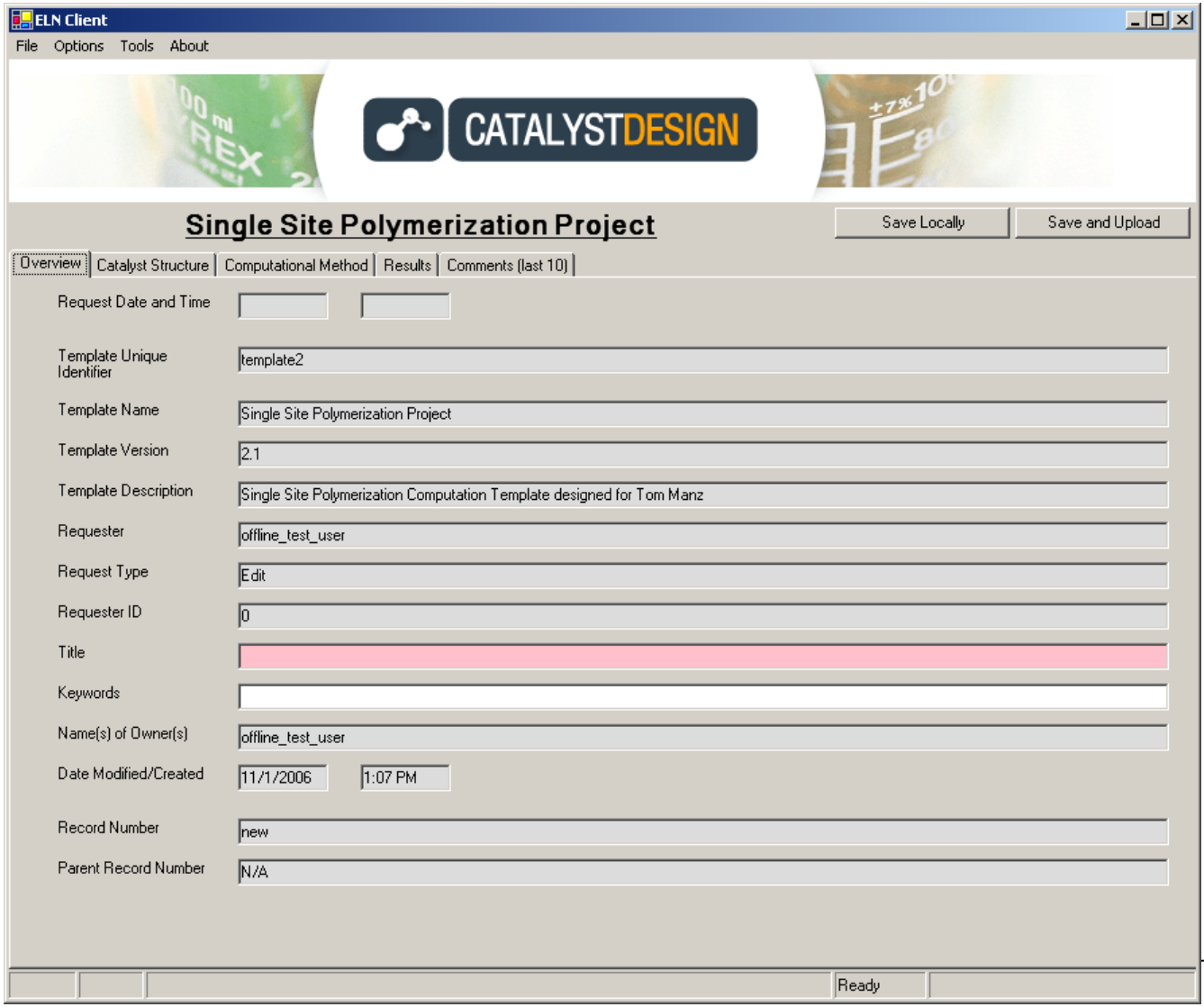


Tabbed layout for Easy Navigation

Color Coded fields tell user what is required

e-Lab Notebook

header | Catalyst Synthesis | Catalyst Characterization | Polymerization | Comments

Performed on: 12/1/2006 1:07 PM

Performed by: Cornel Stanciu

Catalyst Name: anti-(C2H4(1-Ind)2)ZrMe2

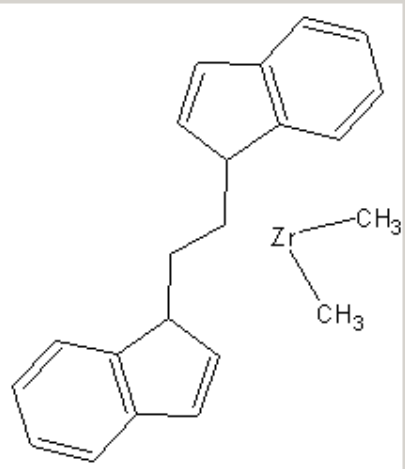
Catalyst InChI String: InChI=1/C20H16.2CH3.Zr/c1-3-7-19-15(5-1)9-11-17(19)13-14-18-12-10-16-6-2-4-8-20(16)18...

Catalyst SMILES string: [Zr]1|2|4|5|7|8|9|%10|%11(C([H])([H])[H])(C([H])([H])[H])[C]:6(:[C]3|1:...

Also Known As: Brintzinger's catalyst; (EBI)ZrMe2

Catalyst Batch Name: 1

Structure Figure: anti-(C2H4(1-Ind)2)ZrMe2.gif



Structure as CML: anti-(C2H4(1-Ind)2)ZrMe2.sk2

Several ways of identifying the catalyst

Including InChI and SMILES

Catalyst structure drawing made with chemsketch

Catalyst structure also attached in chemsketch format for easy editing

e-Lab Notebook

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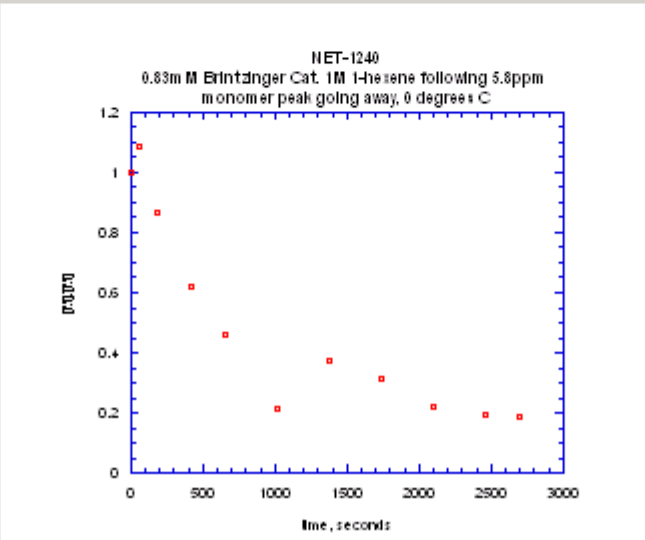
Kinetic Data from NMR

Performed on	2/9/2007 5:09 PM
Performed by	Nicholas Travia
Catalyst Batch Name	1
Instrument	Inova 300
Internal Standard	PH2CH2
Solvent	Toluene-d8
Temperature (C)	25
Kinetic Data	MQ-NET-1240.csv
Image of Kinetic Data	MQ-NET-1240.PNG



Metadata and other details about the experiment

Raw data attached

Short Summary Graph Image

e-Lab Notebook

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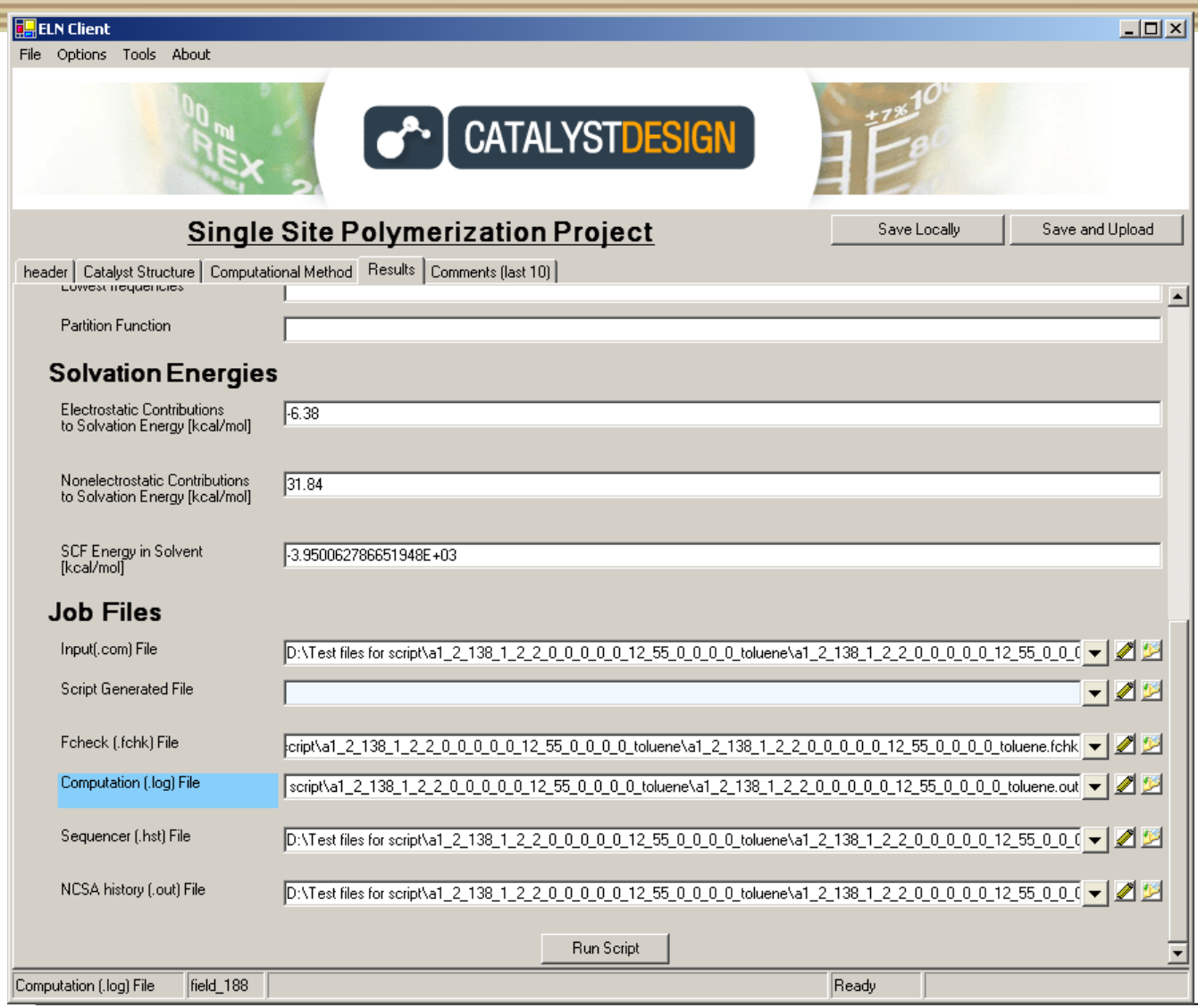

Custom Parser automatically fills out fields from Gaussian Log files

Outline

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- *Data Ingress – e-Lab Notebook*
- *Database – ontologically enabled*
- *Integrated analysis environment*
- *Analysis tools*
- *Visualization*
- *Computer-aided discovery*

Ontologically Enabled Database

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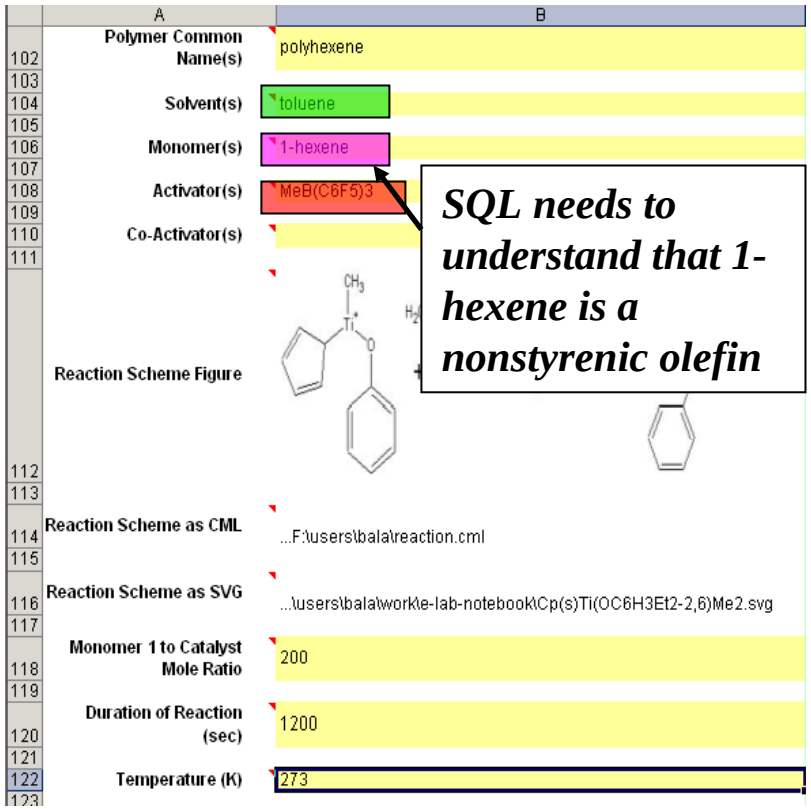
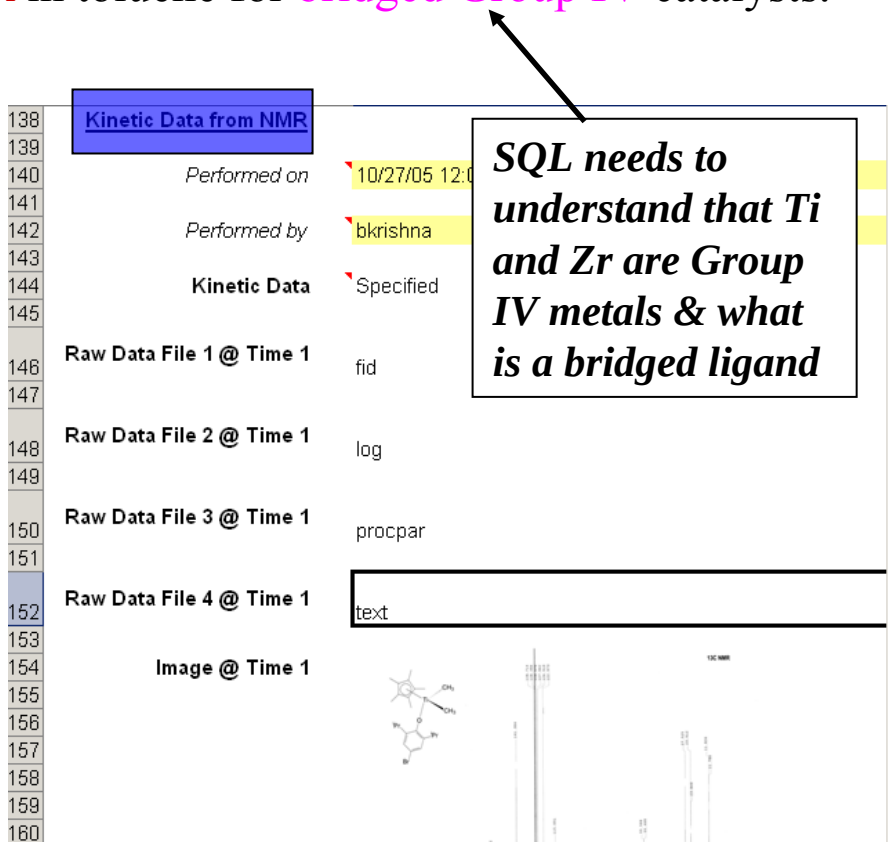
- Consider a database with 10,000 or more records
- Example Query: Find all polymerization data for all non-styrenic olefin monomers for which the kinetics were measured via NMR in toluene for bridged Group IV catalysts.





Ontology: Defines relationships between vocabulary words

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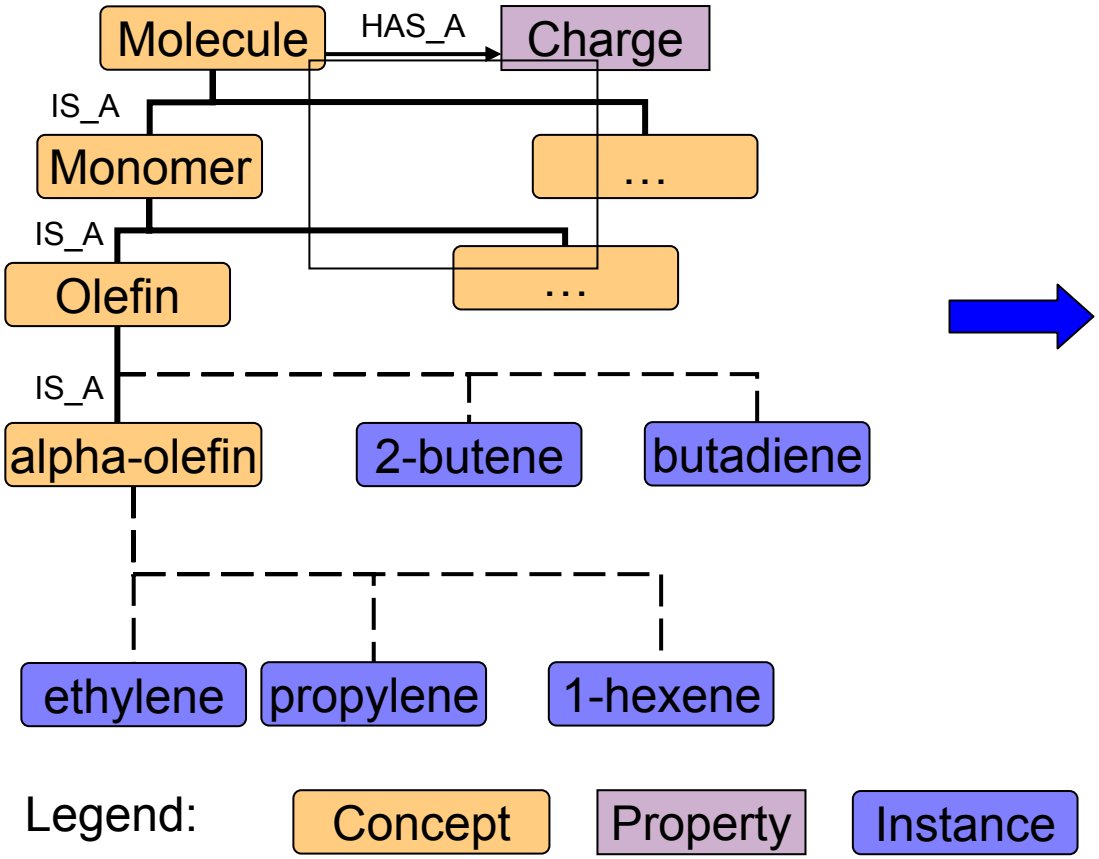
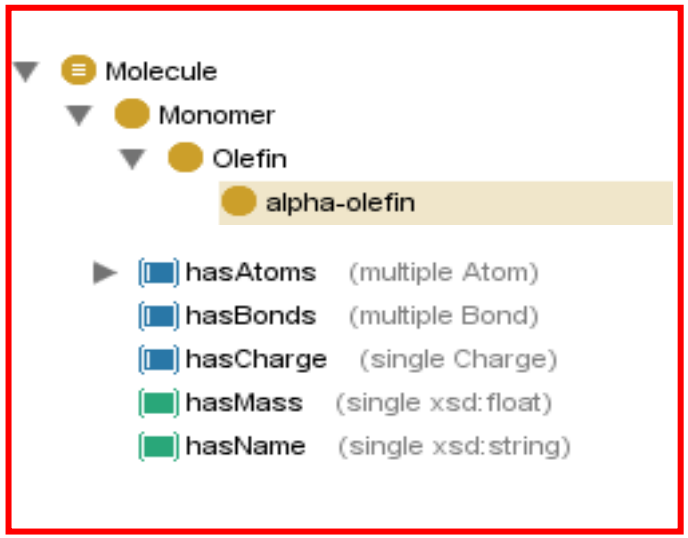
Example ontology for aryloxide chemistry



Protégé screenshot



- ***Web Ontology Language (OWL) is W3C standard***
- ***Encodes logic in Description Logic (DL) format***
- ***Use Protégé as OWL editor***

Ontological-SQL Query Engine

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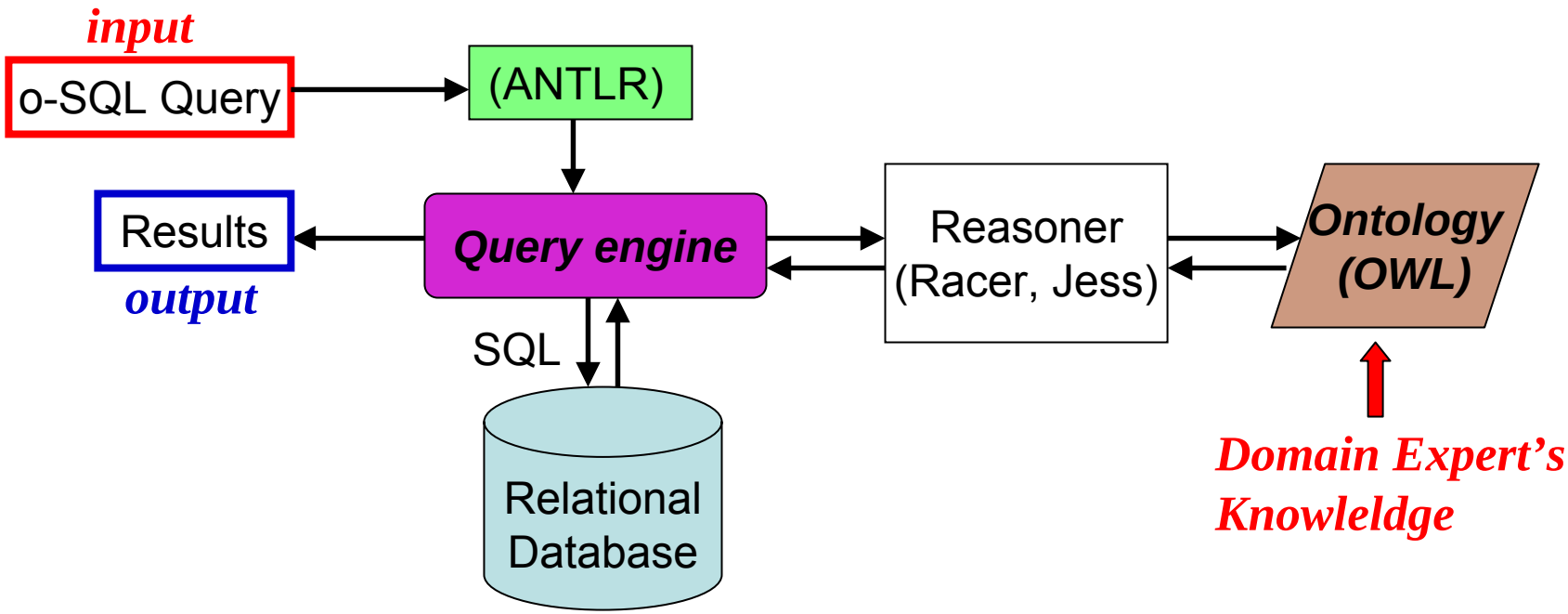
Design: A semantic analysis layer interacts with a data retrieval layer



ANTLR = ANother Tool for Language Recognition : Parser generator
Racer, Jess: classification of concepts and instances in ontology
OWL = Web Ontology Language

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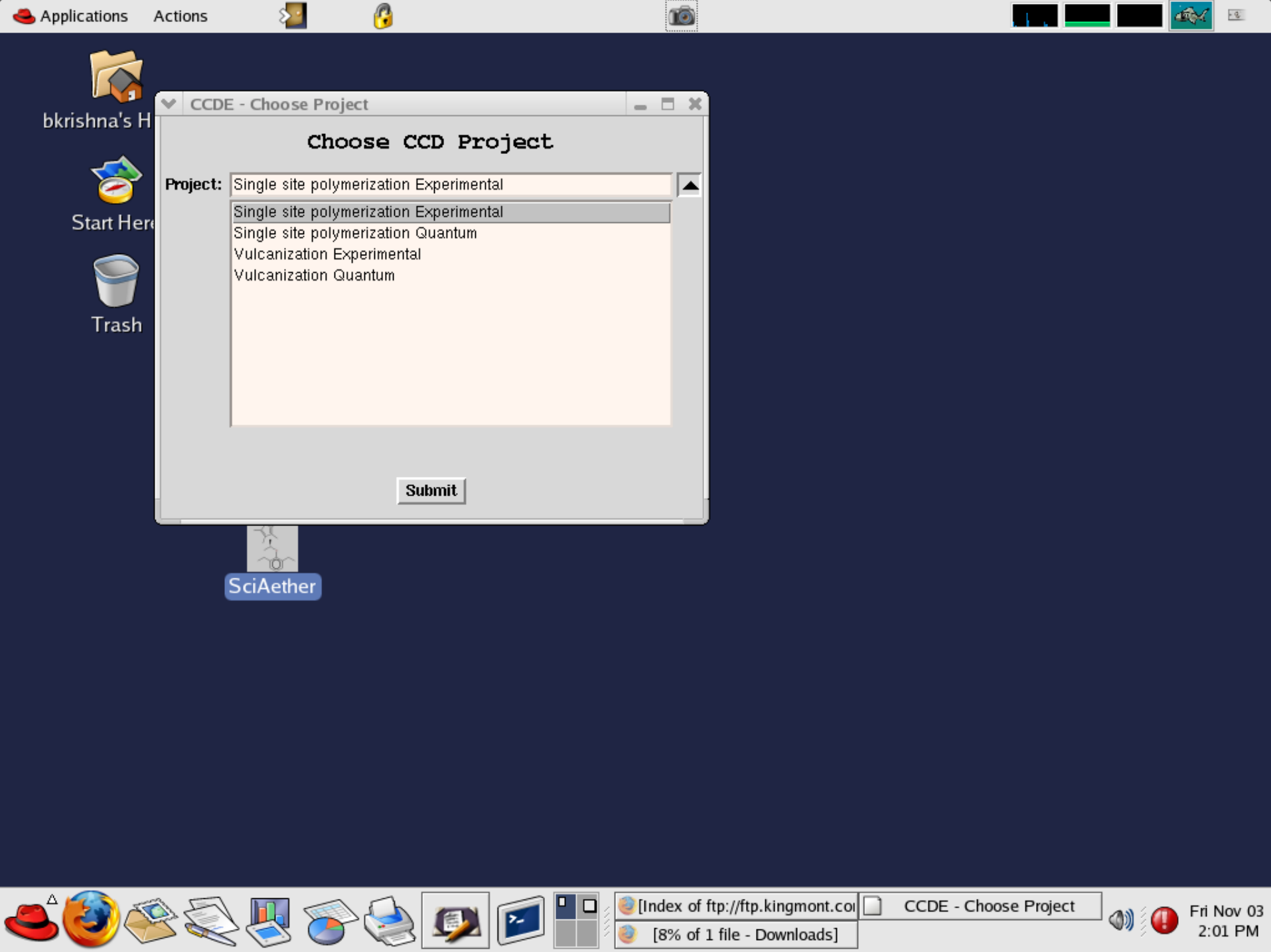
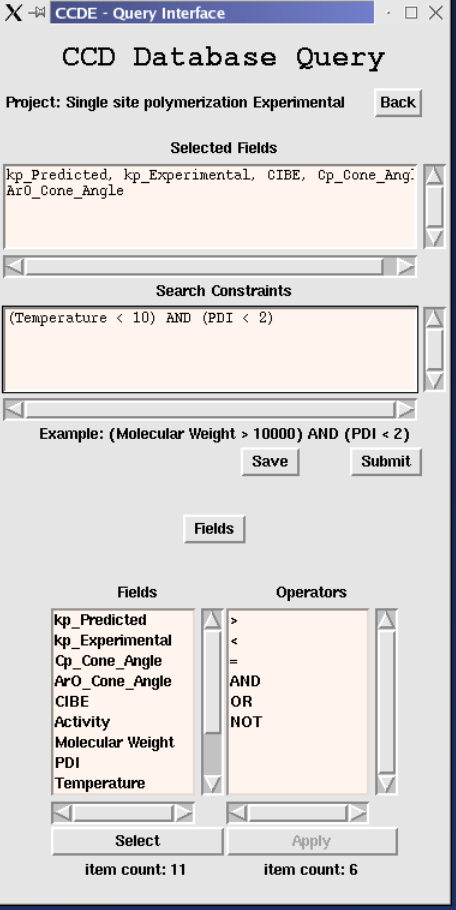

Applications
Actions
bkrishna's H
Start Here
Trash
CCDE - Choose Project
Choose CCD Project
Project:
Single site polymerization Experimental
Single site polymerization Experimental
Single site polymerization Quantum
Vulcanization Experimental
Vulcanization Quantum
Submit
SciAether
[Index of ftp://ftp.kingmont.co
CCDE - Choose Project
[8% of 1 file - Downloads]
Fri Nov 03
2:01 PM


CCDE - Query Interface
CCD Database Query
Project: Single site polymerization Experimental
Back
Selected Fields
kp_Predicted, kp_Experimental, CIBE, Cp_Cone_Ang
ArO_Cone_Angle
Search Constraints
(Temperature < 10) AND (PDI < 2)
Example: (Molecular Weight > 10000) AND (PDI < 2)
Save
Submit
Fields
Fields
Operators
kp_Predicted
kp_Experimental
Cp_Cone_Angle
ArO_Cone_Angle
CIBE
Activity
Molecular Weight
PDI
Temperature
>
<
=
AND
OR
NOT
Select
Apply
item count: 11
item count: 6

CCDE - Query Interface
Run command:
10:25 am

CCDE - Query Interface

CCD Database Query

Project: Single site polymerization Experimental

Back

Selected Fields

kp_Predicted, kp_Experimental, CIBE, Cp_Cone_Ang:
ArO_Cone_Angle

Search Constraints

(Temperature < 10) AND (PDI < 2)

Example: (Molecular Weight > 10000) AND (PDI < 2)

Save Submit

Fields

Fields	Operators
kp_Predicted	>
kp_Experimental	<
Cp_Cone_Angle	=
ArO_Cone_Angle	AND
CIBE	OR
Activity	NOT
Molecular Weight	
PDI	
Temperature	

Select Apply

item count: 11 item count: 6

CCD Table 1

File Edit View Command Help

App

CCD Table

	image	ArO_Cone_Angle	kp_Predicted	kp_Experimental	C
0		97.8	0.23	0.22	35
1		112.3	0.36	0.34	33
2		116.2	0.38	0.42	33
3		66.6	0.39	0.41	30
4		66.6	0.24	0.27	31
5		66.5	0.27	0.24	31
6		66.44	0.27	0.27	31
7		66.4	0.41	0.38	30
8		66.7	0.44	0.46	30
9		97	0.51	0.51	28
10		111.9	0.78	0.78	26
11		114.8	0.99	0.92	26
12		97.9	0.41	0.74	29
13		96.9	0.32	0.28	29
14		82.8	0.27	0.27	20
15		148.1	1.35	1.36	14
16		66.7	0.25	0.24	29
17		66.4	0.19	0.2	30

CCDE - Query Interface

CCD Database Query

Project: Single site polymerization Experimental

Back

Selected Fields

kp_Predicted, kp_Experimental, CIBE, Cp_Cone_Ang:
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Save Submit

Fields

Fields	Operators
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kp_Experimental	<
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PDI	
Temperature	

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CCDE - Query Interface

CCD Database Query

Project: Single site polymerization Experimental Back

Selected Fields

kp_Predicted, kp_Experimental, CIBE, Cp_Cone_Ang:
ArO_Cone_Angle

Search Constraints

(Temperature < 10) AND (PDI < 2)

Example: (Molecular Weight > 10000) AND (PDI < 2)

Save Submit

Fields

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kp_Experimental	<
Cp_Cone_Angle	=
ArO_Cone_Angle	AND
CIBE	OR
Activity	NOT
Molecular Weight	
PDI	
Temperature	

Select Apply

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CCD Table 1

File Edit View Command Help

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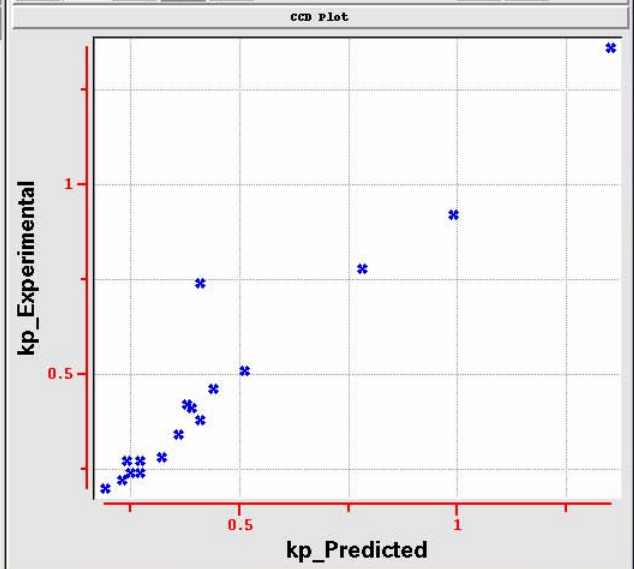
CCD Graph 1

File Edit View AxisChange Command Help

App



CCDE - Query Interface

CCD Database Query

Project: Single site polymerization Experimental Back

Selected Fields

kp_Predicted, kp_Experimental, CIBE, Cp_Cone_Ang:
ArO_Cone_Angle

Search Constraints

(Temperature < 10) AND (PDI < 2)

Example: (Molecular Weight > 10000) AND (PDI < 2)

Save Submit

Fields

Fields	Operators
kp_Predicted	>
kp_Experimental	<
Cp_Cone_Angle	=
ArO_Cone_Angle	AND
CIBE	OR
Activity	NOT
Molecular Weight	
PDI	
Temperature	

Select Apply

item count: 11 item count: 6

CCD Table 1

File Edit View Command Help

App

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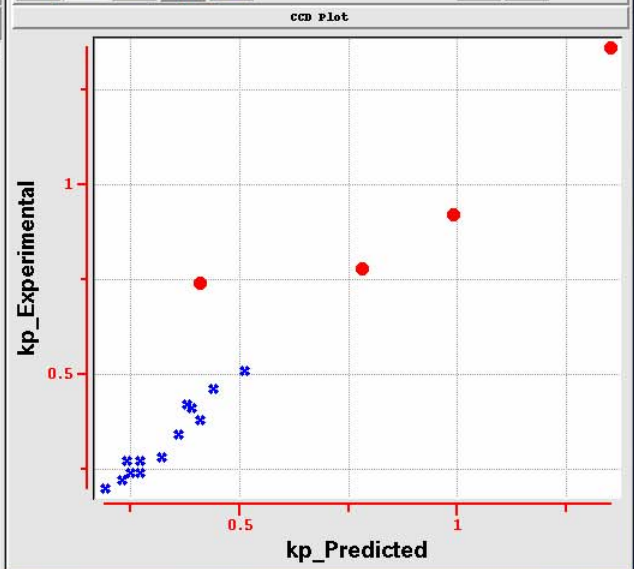
CCD Graph 1

File Edit View AxisChange Command Help

App



CCDE - Query Interface
CCD Table 1
CCD Graph 1
Run command:
10:29 am

CCDE - Query Interface

CCD Database Query

Project: Single site polymerization Experimental Back

Selected Fields

kp_Predicted, kp_Experimental, CIBE, Cp_Cone_Ang:
ArO_Cone_Angle

Search Constraints

(Temperature < 10) AND (PDI < 2)

Example: (Molecular Weight > 10000) AND (PDI < 2)

Save Submit

Fields

Fields	Operators
kp_Predicted	>
kp_Experimental	<
Cp_Cone_Angle	=
ArO_Cone_Angle	AND
CIBE	OR
Activity	NOT
Molecular Weight	
PDI	
Temperature	

Select Apply

item count: 11 item count: 6

CCD Table 1

File Edit View Command Help

App

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	image	ArO_Cone_Angle	kp_Predicted	kp_Experimental	C
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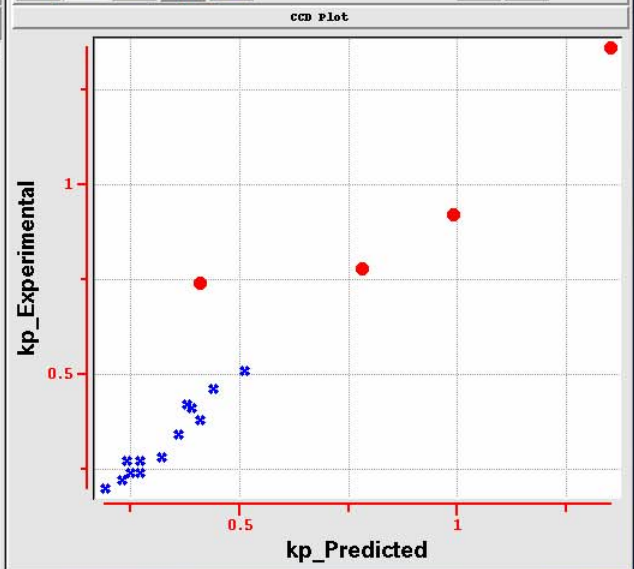
CCD Graph 1

File Edit View AxisChange Command Help

App



CCD Table 1 <2>

File Edit View Command Help

App

CCD Table

	image	ArO_Cone_Angle	kp_Predicted	kp_Exper
10		111.9	0.78	0.78
11		114.8	0.99	0.92
12		97.9	0.41	0.74
15		148.1	1.35	1.36

CCDE - Query Interface | CCD Graph 1 | CCD Table 1 | CCD Table 1 <2>

Run command:

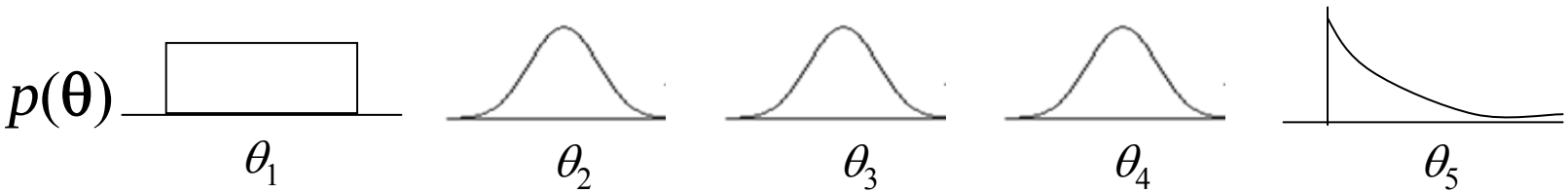
10:32 am

Outline

- *Data Ingress – e-Lab Notebook*
- *Database – ontologically enabled*
- *Integrated analysis environment*
- *Analysis tools*
  - *Commercial Packages (MatLab, JMP, etc.)*
  - *Personal Codes (MatLab, C++, Fortran, etc.)*
  - *Nonlinear Bayesian Statistics*
  - *Domain specific tools*
- *Visualization*
- *Computer-aided discovery*

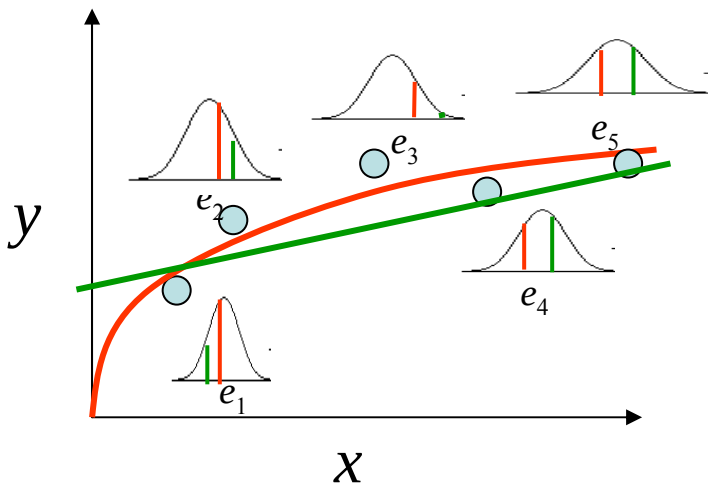
Parameter Estimation

- Expert knowledge (Prior probability distribution)



$$p(\boldsymbol{\theta}) = p(\theta_1)\,p(\theta_2)\cdots p(\theta_n)$$

- Likelihood function, $L(\text{data}|\boldsymbol{\theta})$



$$L(\text{data}\,|\,\boldsymbol{\theta}) = p(e_1)\,p(e_2)\cdots p(e_n)$$

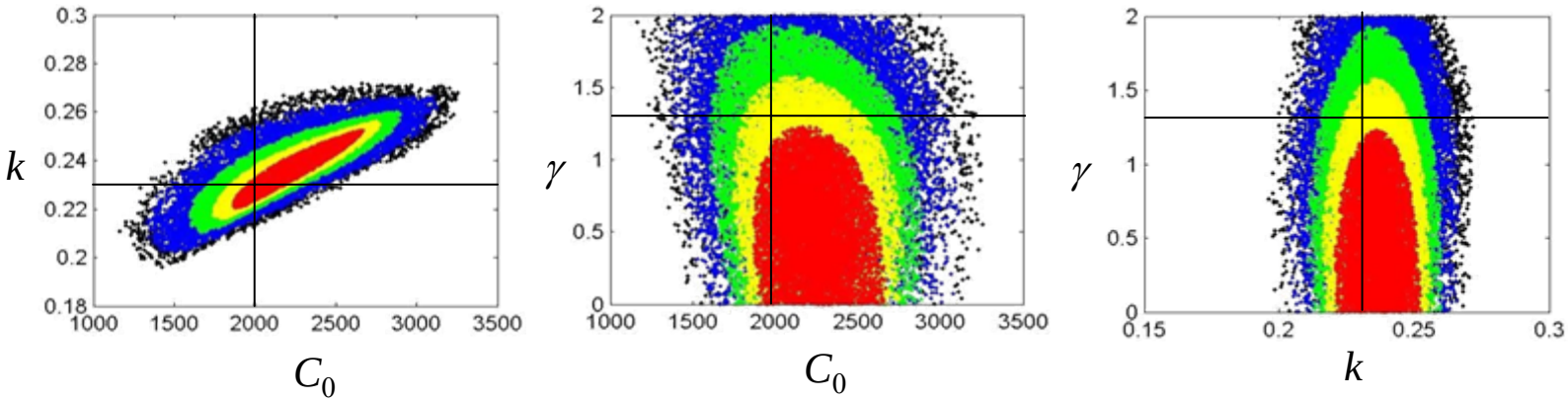
- Both expert knowledge and data fitting are important
- How to compromise these two different types of information to obtain the most reasonable parameter estimates?

The larger, the better

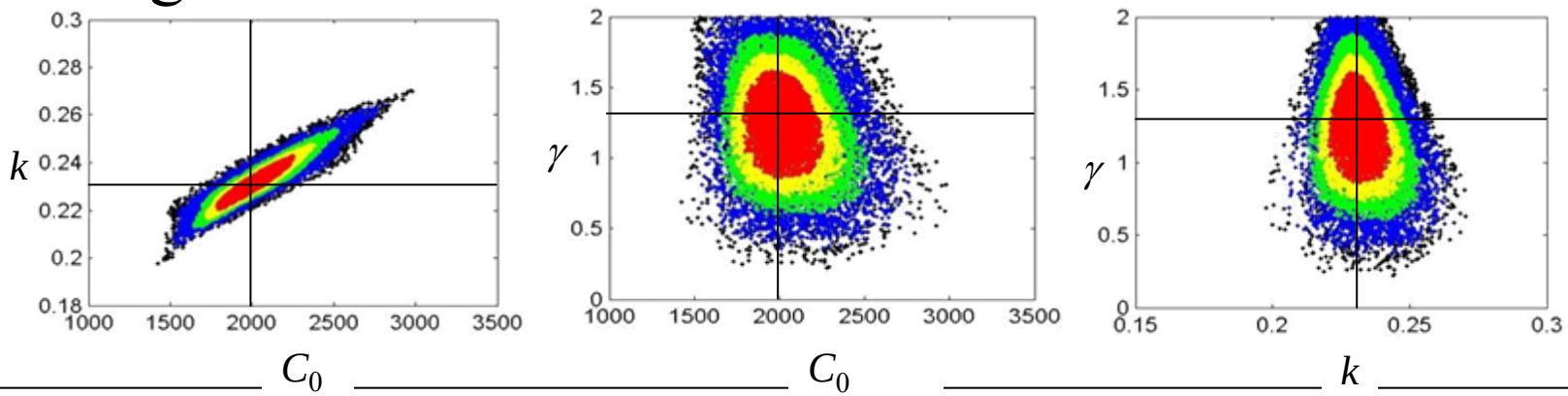
Revisit the Example

$$C_i = C_0 \exp(-kt_i) + \varepsilon_i \quad C_0 = 2000,\ k = 0.23,\ \gamma = 1.3$$

- Non-designed data set



- Designed data set



Outline

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- *Data Ingress – e-Lab Notebook*
- *Database – ontologically enabled*
- *Integrated analysis environment*
- *Analysis tools*
- *Visualization*
- *Computer-aided discovery*

Rich Graphics

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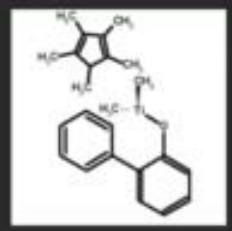
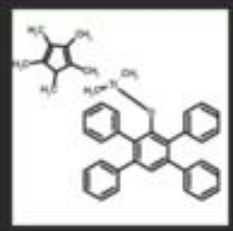
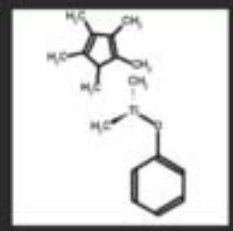
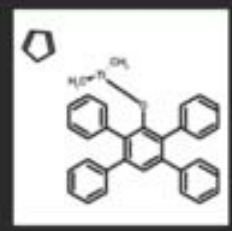
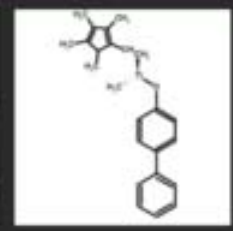
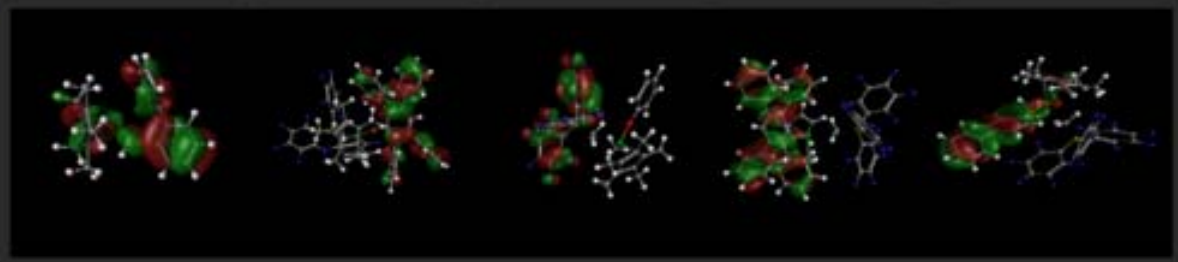
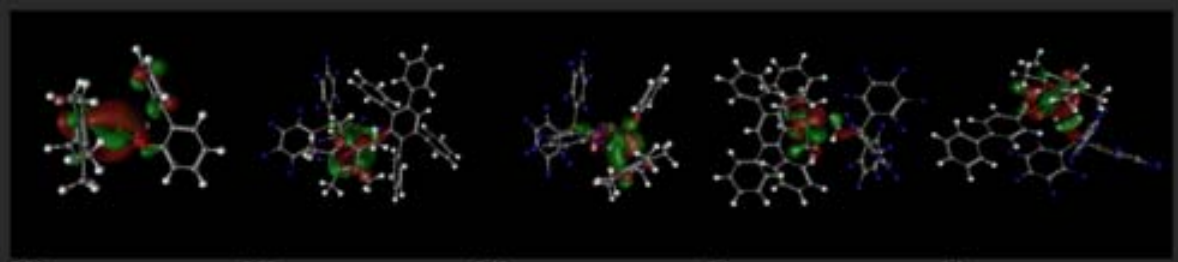
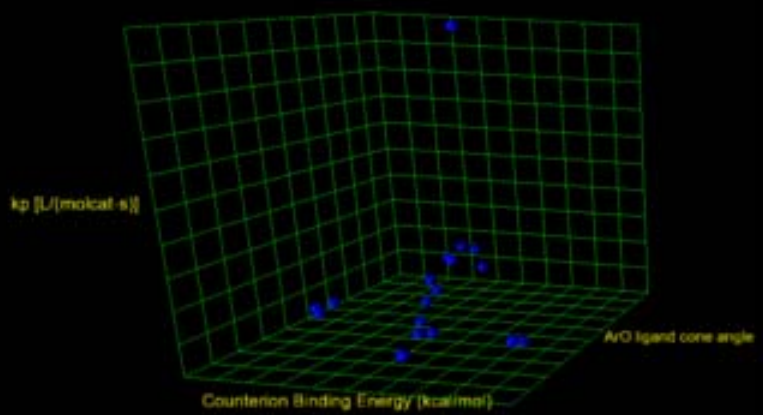
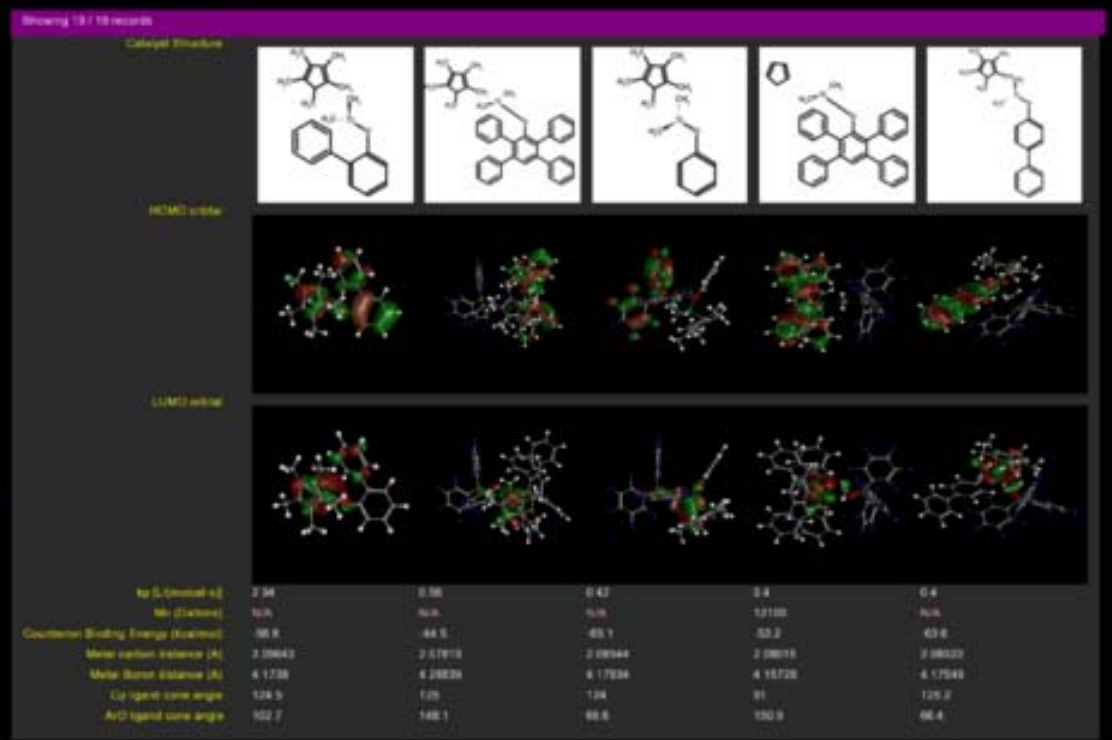
Showing 19 / 19 records

Catalyst Structure					
HOMO orbital					
LUMO orbital					
kp [L/(molcat·s)]	2.94	0.56	0.42	0.4	0.4
Mn (Daltons)	N/A	N/A	N/A	12100	N/A
Counterion Binding Energy (kcal/mol)	-56.6	-44.5	-65.1	-53.2	-63.6
Metal-carbon distance (A)	2.09643	2.07819	2.08544	2.08015	2.08533
Metal-Boron distance (A)	4.1738	4.26839	4.17634	4.15728	4.17549
Cp ligand cone angle	124.5	125	124	91	125.2
ArO ligand cone angle	102.7	148.1	66.6	150.9	66.4


kp [L/(molcat·s)]
ArO ligand cone angle
Counterion Binding Energy (kcal/mol)


Catalyst Structure
HOMO orbital
LUMO orbital

Natural Representation of Data

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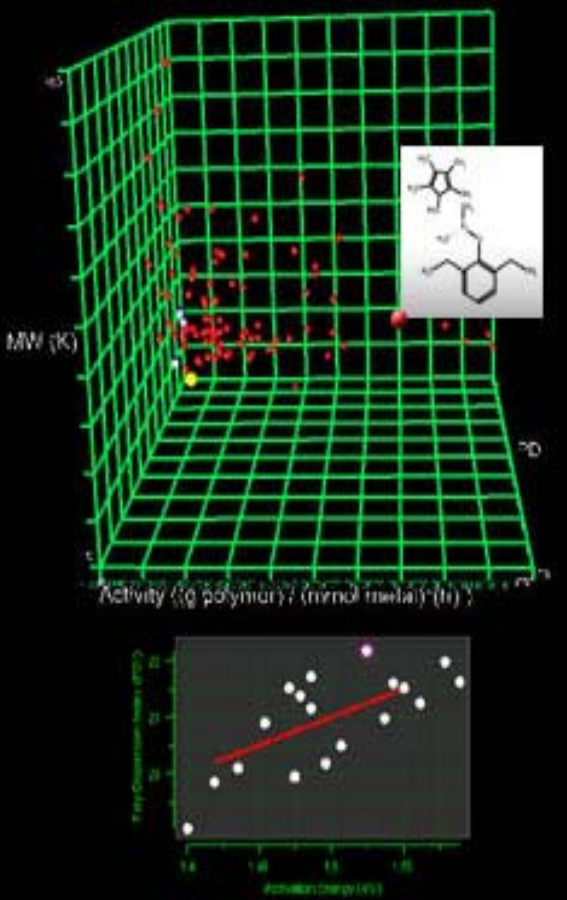

Showing 20 records of 20

Molecule	A0	A0	A0	A0	A0
Conformer	1	2	3	4	5
3D View					
Symbol					
E (hartree)	-2240.58	-2240.58	-2240.58	-2240.58	-2240.58
G at 148 °C (hartree)	-2240.47	-2240.47	-2240.47	-2240.47	-2240.47
HOMO energy (hartree)	-0.234	-0.234	-0.235	-0.234	-0.234
LUMO energy (hartree)	-0.076	-0.076	-0.061	-0.076	-0.076
HOMO-LUMO gap (hartree)	0.158	0.158	0.174	0.158	0.158
SOMO energy (hartree)	N/A	N/A	N/A	N/A	N/A
BDE S-S (kcal/mol)	34.2076	34.2076	34.7432	34.2076	34.2076
BDE C-S kcal/mol	62.0855	62.0855	62.621	62.0855	62.0855
K S-S (kcal/mol)	6.77761e-09	6.78313e-09	2.57265e-09	6.78845e-09	6.78845e-09

Summary

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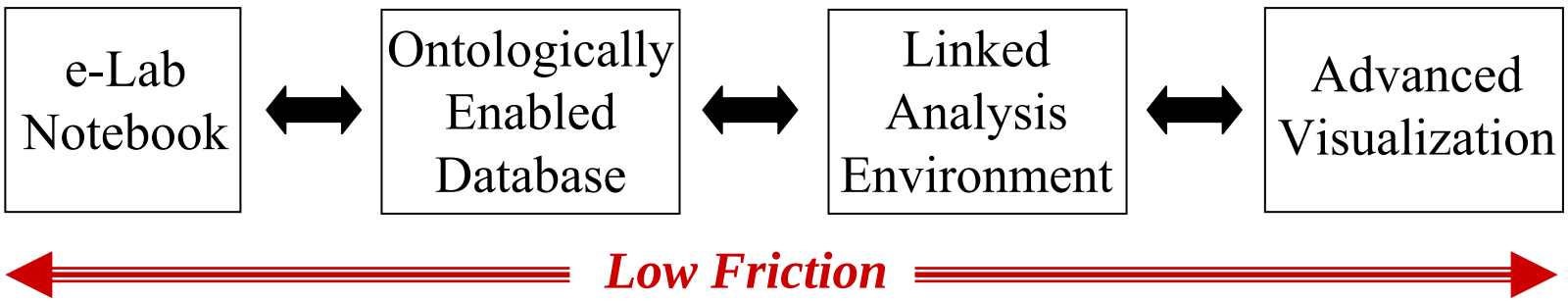
- ***SciAether – prototype cyberinfrastructure***
  - ***Initially developed for catalysis science***
  - ***Can be expanded to include a wide range of chemistry/materials/biology research***
- ***Scaleable components***



- ***Minimum system requirements***

	Academic Cost	
– ***PC with Windows XP***	***$ 1,200***	
– ***Microsoft Office***	***100***	***(free)***
– ***Database (MS Access or DB2 or ….)***	***50***	***(free)***
– ***ChemSketch – freeware version***	***free***	
– ***Analysis software (MatLab, etc. – user's choice)***	***???***	***(free)***

Outline

PURDUE UNIVERSITY

- ***Data Ingress – e-Lab Notebook***
- ***Database – ontologically enabled***
- ***Integrated analysis environment***
- ***Analysis tools***
- ***Visualization***
- ***Computer-aided discovery***

Does it work?

1- Hexene Polymerization by Titanium Catalysts with Phenoxy based ligands

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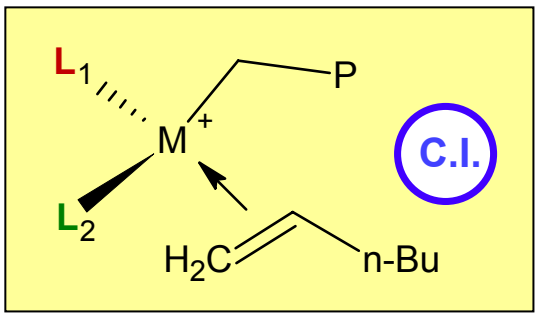
A large number of available substituted phenols allow tunability of steric and electronic variation of the catalyst.

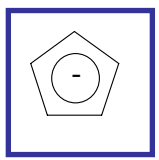


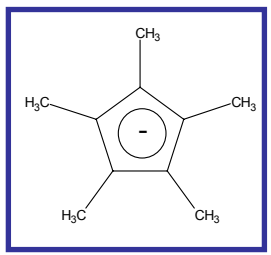
M = Ti, Zr, Hf

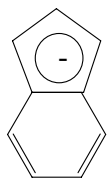
C.I. = $[MeB(C_6F_5)_3]^-$

$[B(C_6F_5)_4]^-$

$L_1 = \{$



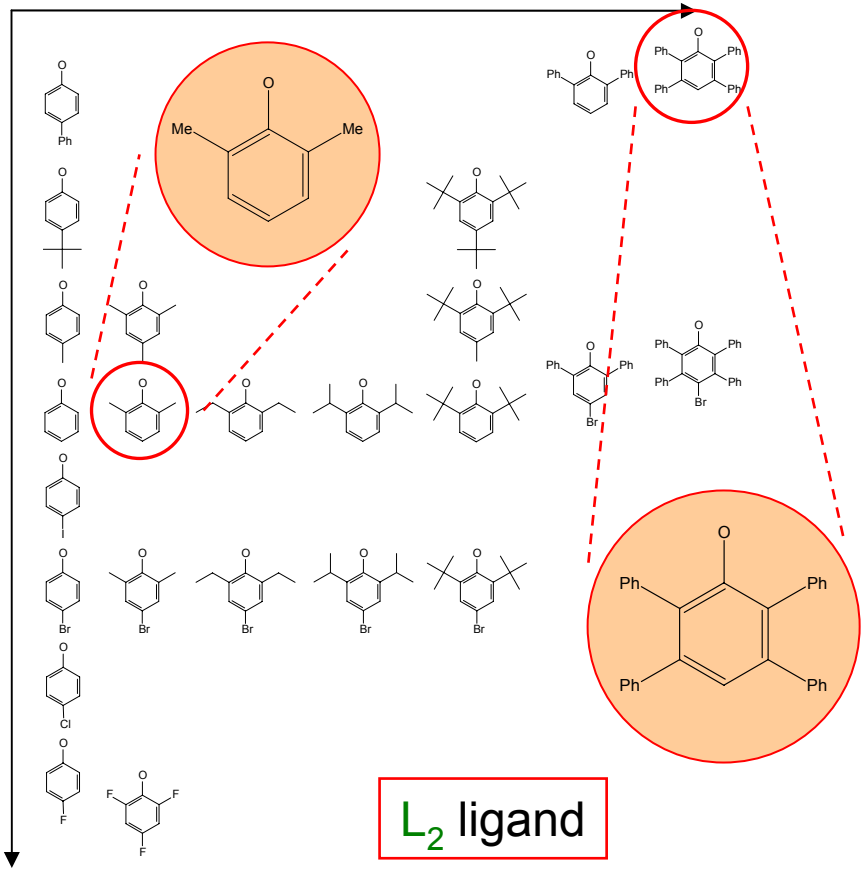




$\}$

Steric

Electronic



Effect of Aryloxide Ligand on Propagation Rate for Titanium Catalyst

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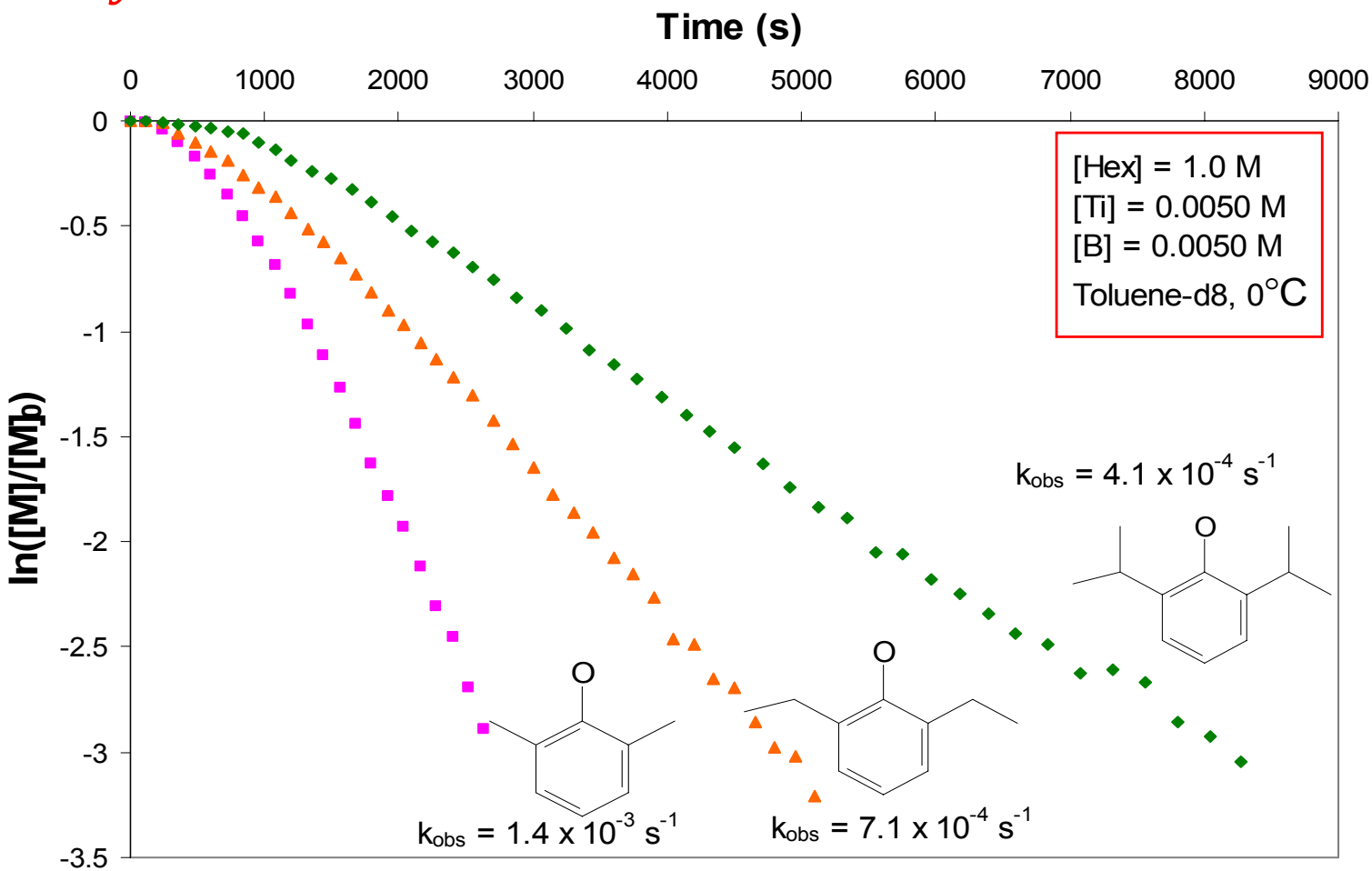
Batch Polymerization



Micro-Kinetic Analysis of Olefin Polymerization

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Homo-polymerization Kinetics

* **Initiation** $C + M \xrightarrow{k_i} R_1$
* **Propagation** $R_i + M \xrightarrow{k_p} R_{i+1}$
* **2,1-misinsertion** $R_i + M \xrightarrow{k_{p_{2,1}}} P_{i+1}$
* **Propagation after 2,1-misinsertion** $P_i + M \xrightarrow{k_{p_{2,1\to1,2}}} R_{i+1}$
* **Chain transfer to monomer**
  $R_i + M \xrightarrow{k_{tm}} D_i + R_1$
  $P_i + M \xrightarrow{k_{tm}} D_i + R_1$
* **β hydride chain transfer**
  $R_i \xrightarrow{k_{t\beta}} D_i + C$
  $P_i \xrightarrow{k_{t\beta}} D_i + C$

where C activated catalyst
M monomer
Ri living polymer chain
Pi dormant polymer chain
Di terminated polymer chain (i = 1,2……)

Population Balances

* **For active sites**

$$\frac{dC}{dt} = -k_i \cdot C \cdot M + k_{t\beta} \cdot \left(\sum_1^\infty R_i + \sum_2^\infty P_i \right)$$

* **For living chains of unit length**

$$\frac{dR_1}{dt} = k_i \cdot C \cdot M - (k_p + k_{p_{2,1}}) \cdot M \cdot R_1 + k_{tM} \cdot M \cdot \left(\sum_2^\infty R_i + \sum_2^\infty P_i \right) - k_{t\beta} \cdot R_1$$

* **For living chains with length i**

$$\frac{dR_i}{dt} = k_p \left(R_{i-1} - R_i \right) \cdot M - k_{p_{2,1}} \cdot R_i \cdot M + k_{p_{2,1\to1,2}} \cdot P_{i-1} \cdot M - (k_{tM} \cdot M - k_{t\beta}) \cdot R_i$$

* **For monomer**

$$\frac{dM}{dt} = -k_i \cdot C \cdot M - (k_p + k_{p_{2,1}}) \cdot M \cdot \sum_1^\infty R_i - k_{p_{2,1\to1,2}} \cdot M \cdot \sum_2^\infty P_i - k_{tM} \left(\sum_2^\infty R_i + \sum_2^\infty P_i \right) \cdot M + k_{t\beta} \cdot R_1$$

* **For living chains after 2,1-misinsertion with length i**

$$\frac{dP_i}{dt} = k_{p_{2,1}} \cdot R_{i-1} \cdot M - k_{p_{2,1\to1,2}} \cdot P_i \cdot M - (k_{tM} \cdot M - k_{t\beta}) \cdot P_i$$

* **For terminated chains of length i**

$$\frac{dD_i}{dt} = k_{tM} \cdot M \cdot (R_i + P_i) + k_{t\beta} \cdot (R_i + P_i)$$

DFT Simulation of Propagation Step

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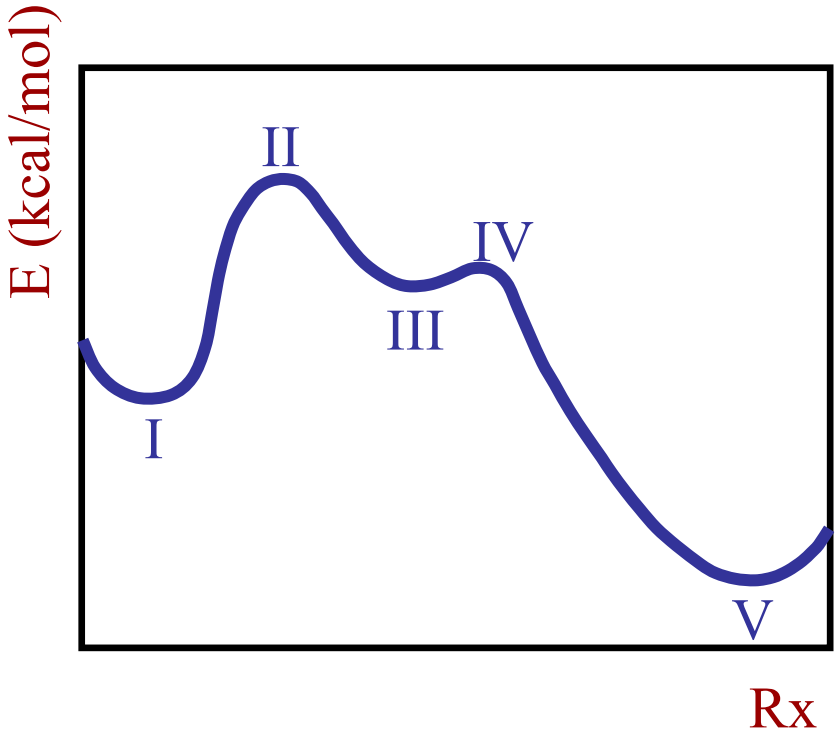
- Backside insertion of 1-hexen into $[CpTi(OC_6H_3Me_2\text{-}2,6)Me^+][MeB(C_6F_5)_3^-]$; OLYP/LALNL2DZ level calculation



I – Reactants E_I=0

II – TS1 E_{II}=17.9

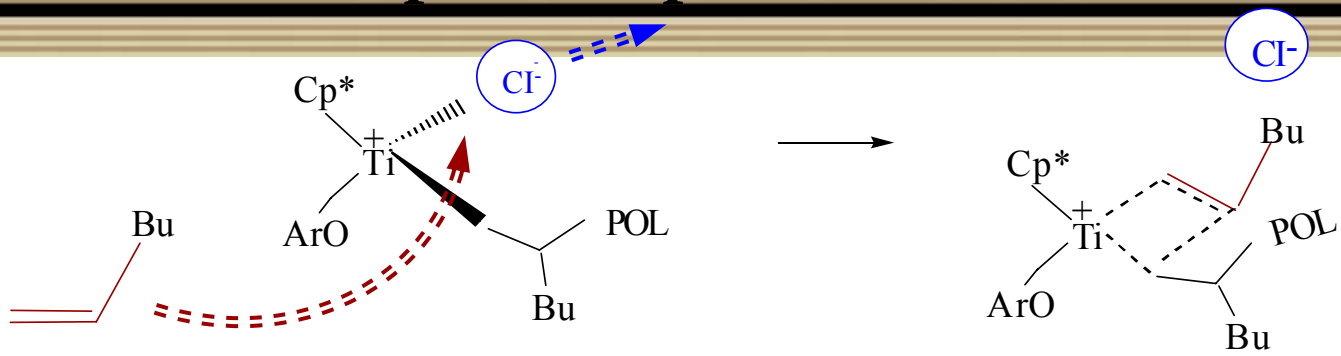
III – Coordinated π-complex E_{III}=12.0

IV – TS2 E_{IV}=13.2

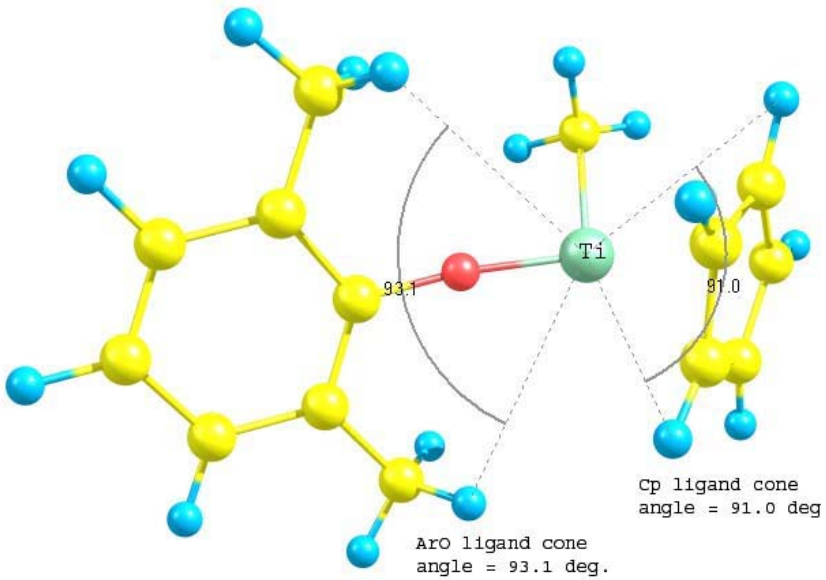
V – Products E_V=-18.8

Conclusion: adsorption is the rate determining step

Postulated mechanics for propagation: Adsorption step



Descriptor #1 – ArO ligand cone angle



Descriptor #2 – CI binding energy

$$\text{CI B.E.} = E\left[\text{Cp}^*\text{–Ti(ArO)(CH}_3\text{)–Cl}^-\right] - \left\{E\left[\text{Cp}^*\text{–Ti(ArO)(CH}_3\text{)}\right] + E\left[\text{Cl}^-\right]\right\}$$

k_p Prediction Model

(Manz, et al. JACS-Communication, 2007)

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$$k_{pred} = k_0 e^{-Ea/RT} = \gamma a_0 e^{-E0/RT} e^{-\alpha EIPS/RT}$$
$$\gamma = 1 - \sin^2(\theta_{Cp'}/4) - \sin^2(\theta_{OAr}/4) - f$$

Predictive Model

α = 0.300, f = 0.187, and the following values of A (M^{-1} s^{-1}) according to catalyst family: (A) 3.01×10^8 (■), (B) 5.22×10^7 (●), (C) A = 2.65×10^7 (◆), (D) 6.88×10^5 (✳), and (E) 1.77×10^7 (▲).

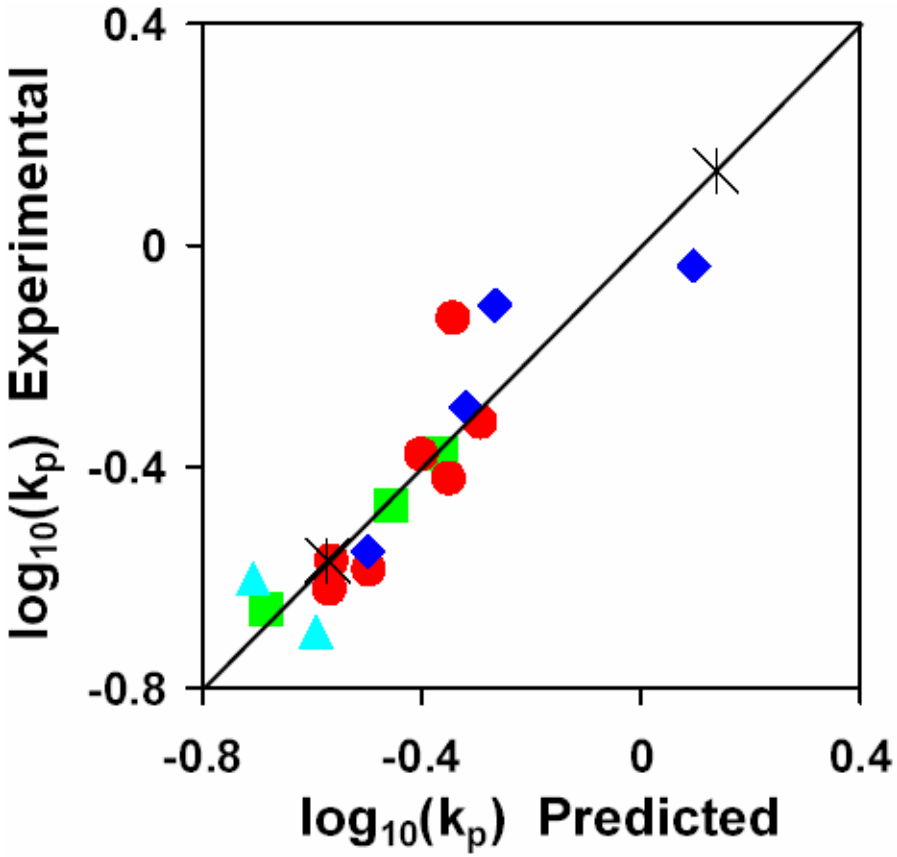
Insight from analysis

↓

Postulate 'hot' catalysis

↓

Synthesized, and catalyst ~2x hotter than reported catalysts



Future Plans

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- ***System has been designed and implemented using commercial software development tools/practices/people***
- ***Expanding usage of SciAether to other groups at Purdue***
- ***Additional capabilities under-development***
  - ***Template Designer for eLN***
  - ***Drop down menus for eLN***
  - ***Expanded ontologies with user GUI for addition of terms***
  - ***Connect to other databases like PubChem via Web Services***
  - ***Direct connection to eLN from analysis environment***
  - ***3D visualization inside of linked analysis environment***
- ***Looking for a few development partners***

www.sciaether.org

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