Modifying catalytic sustainability: aromaticity, conceptual DFT and steric mapping

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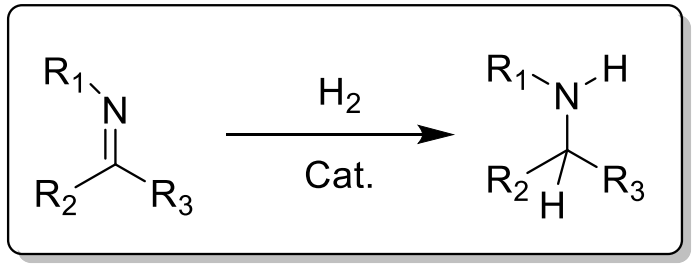
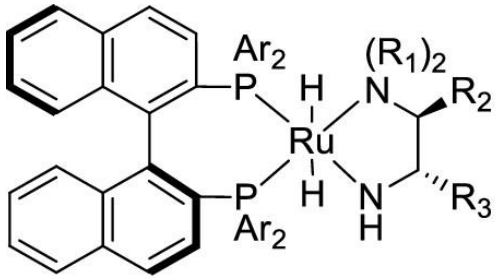
INTRODUCTION

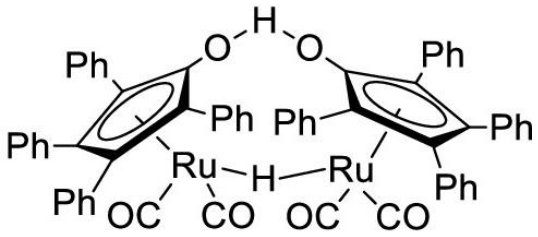
Catalytic hydrogenation



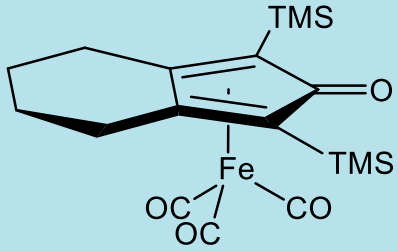
Long-stablished catalysts



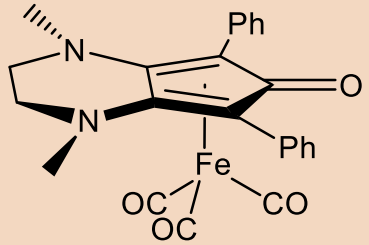
Shvo catalyst



Noyori catalyst



Knölker catalyst

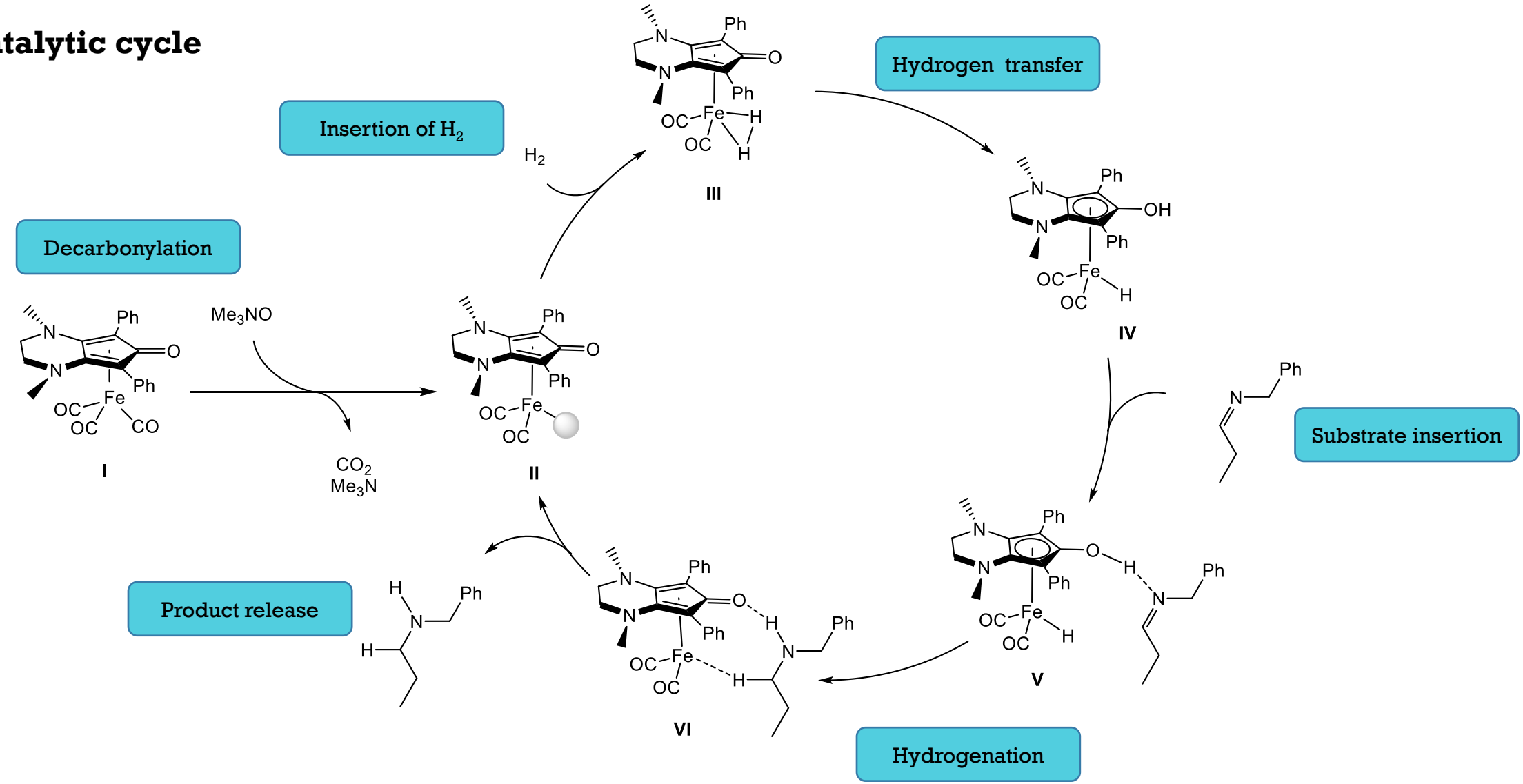


Renaud catalyst

Org. Biomol. Chem., **2006**, *4*, 393-406
J. Am. Chem. Soc., **1986**, *108*, 7400-7402
Angew. Chem. Int. Ed., **1999**, *38*, 2064-2066
J. Am. Chem. Soc., **2009**, *131*, 2499-2507

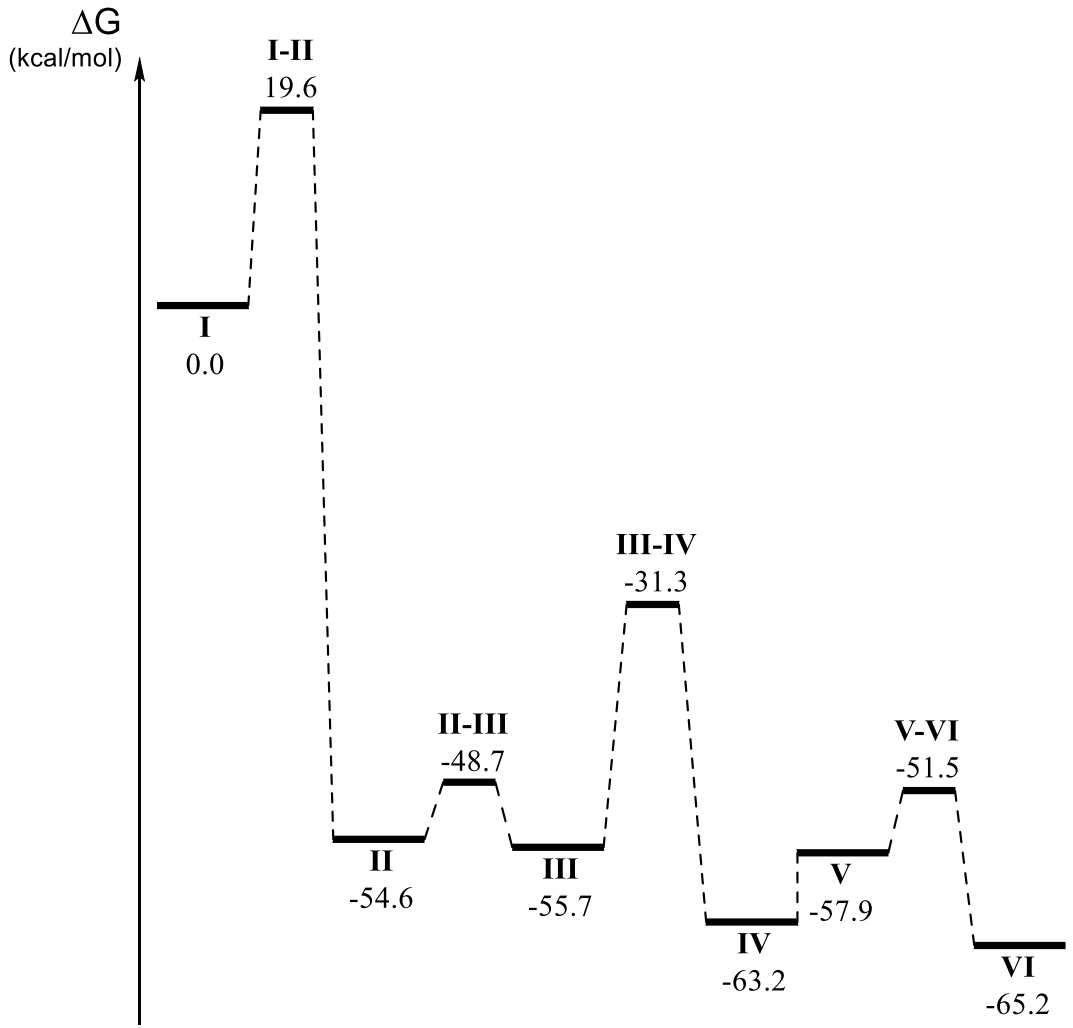
INTRODUCTION

Catalytic cycle

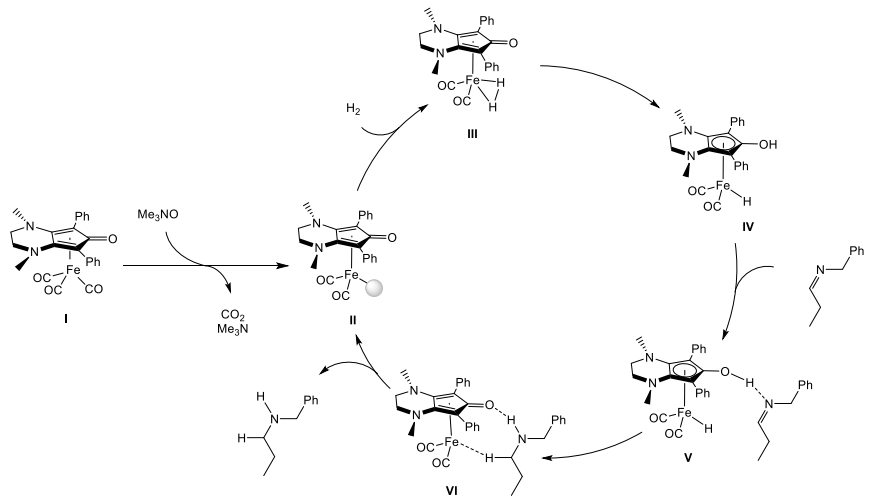


Chem. Eur. J., **2013**, *19*, 17881–17890.

INTRODUCTION

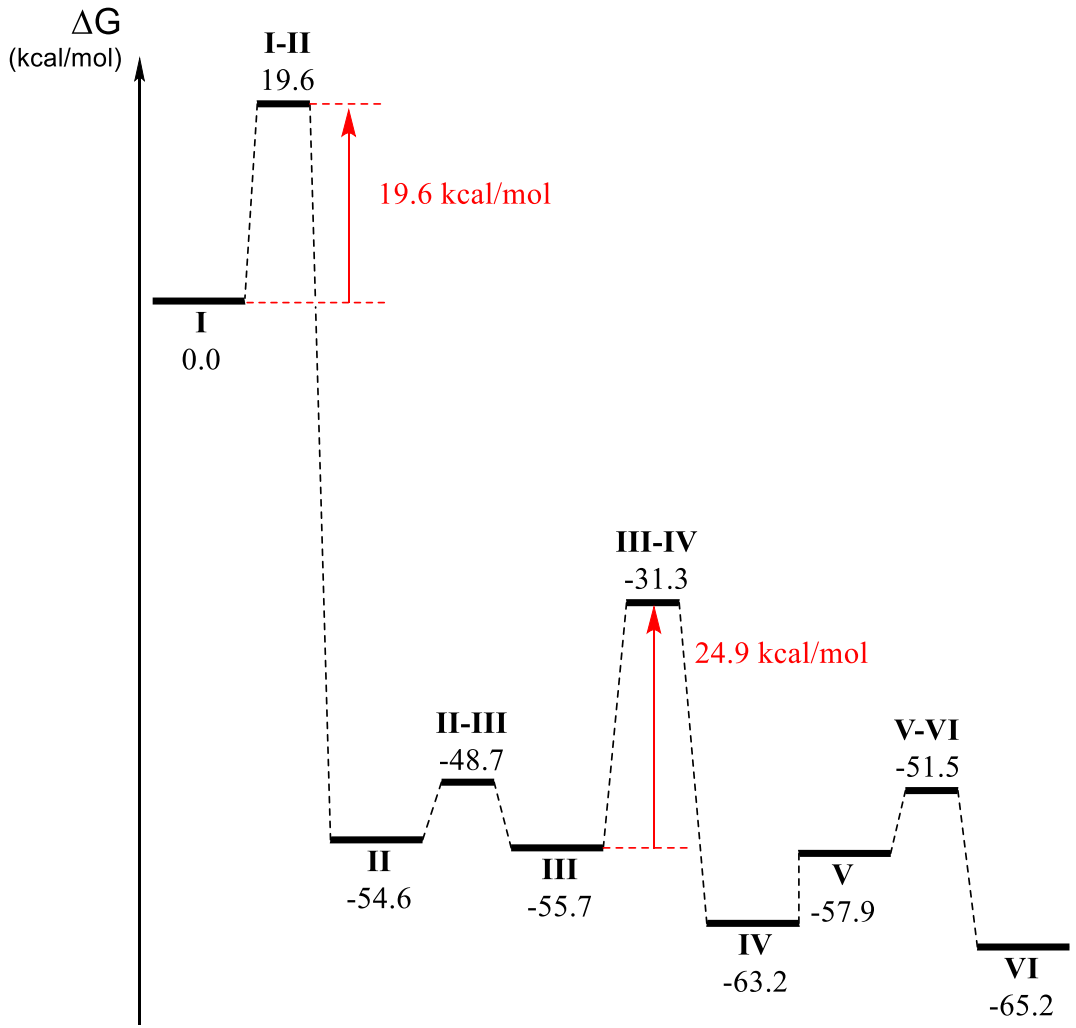


Rate determining step (rds)



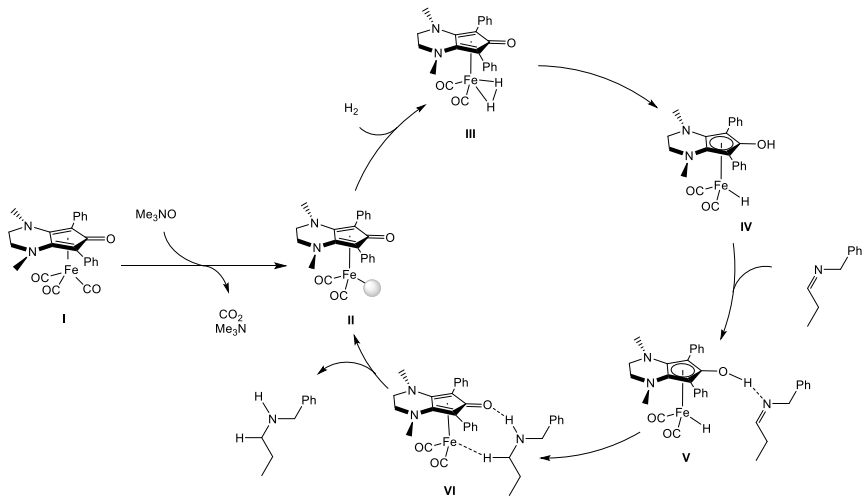
Chem. Eur. J., **2013**, *19*, 17881–17890.

INTRODUCTION



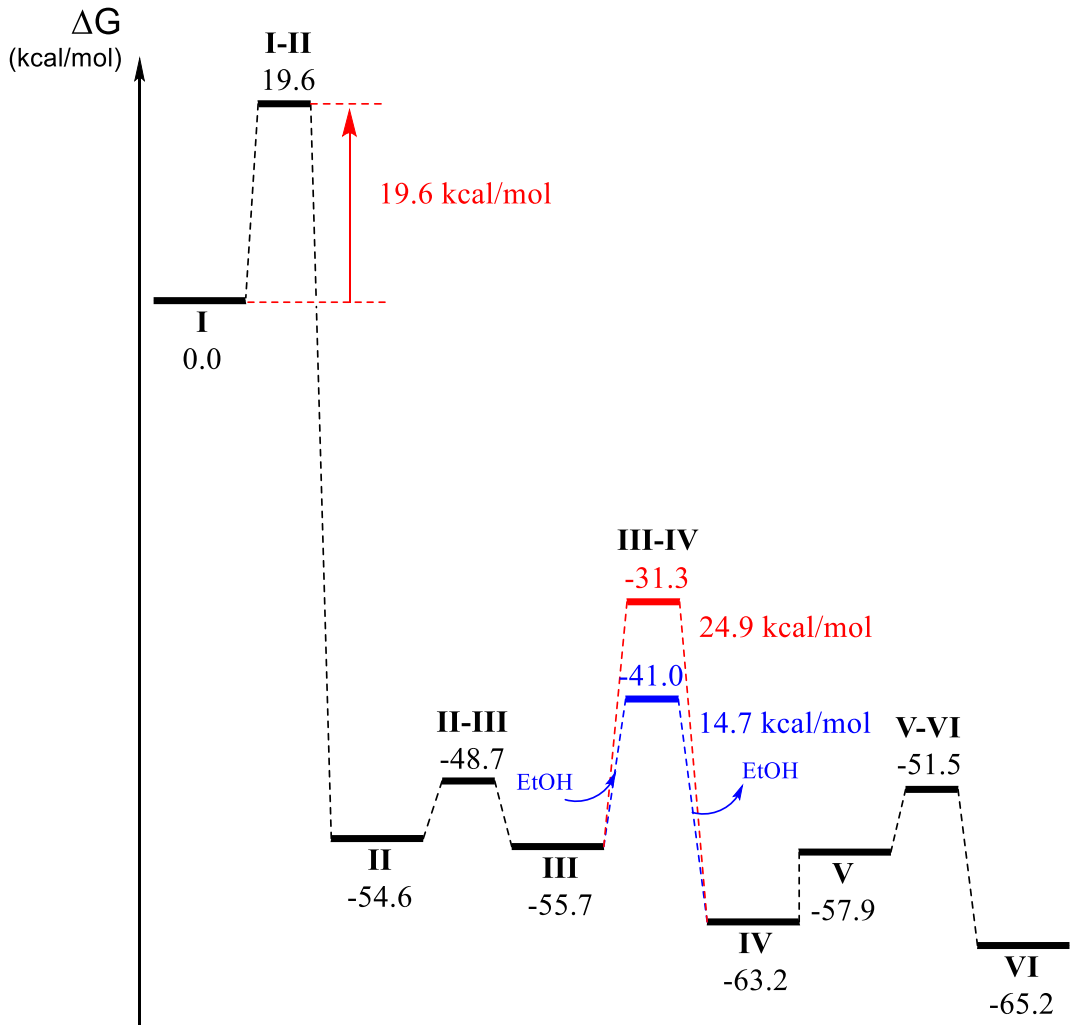
Rate determining step (rds)

- Activation of the catalyst: 19,6 kcal/mol
- Hydrogen transfer: 24,4 kcal/mol



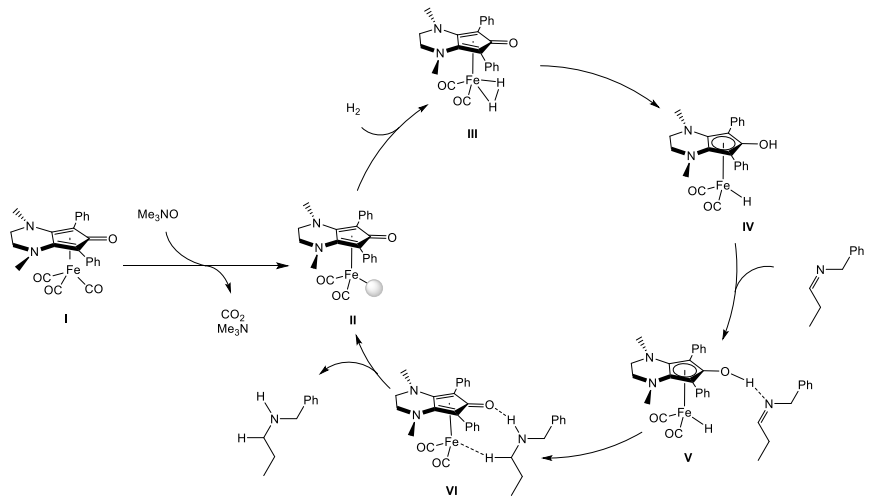
Chem. Eur. J., **2013**, *19*, 17881–17890.

INTRODUCTION



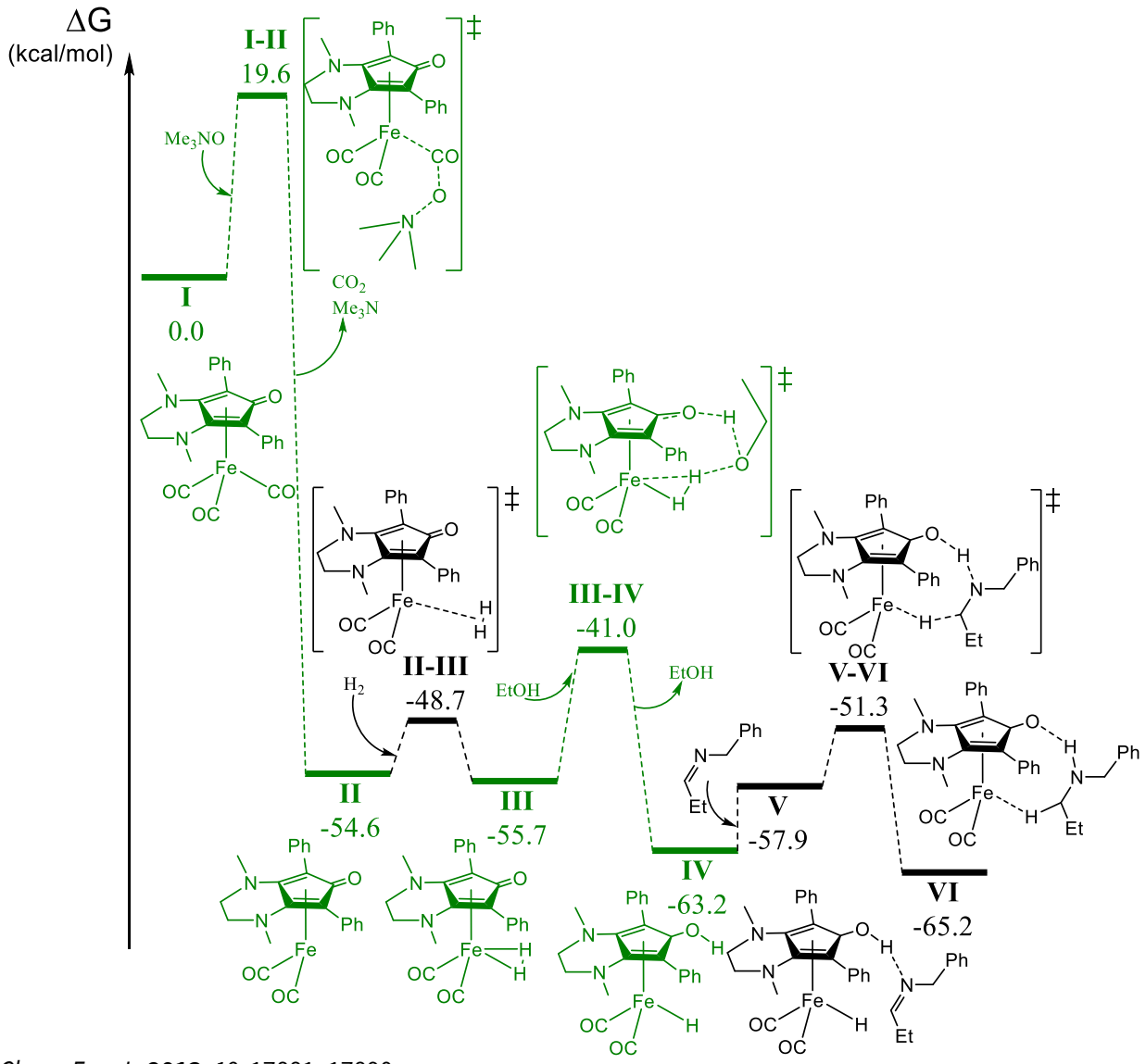
Rate determining step (rds)

- Activation of the catalyst: 19,6 kcal/mol
- ~~Hydrogen transfer: 24,4 kcal/mol~~
- Hydrogen transfer: 14,7 kcal/mol



Chem. Eur. J., **2013**, *19*, 17881–17890.

INTRODUCTION



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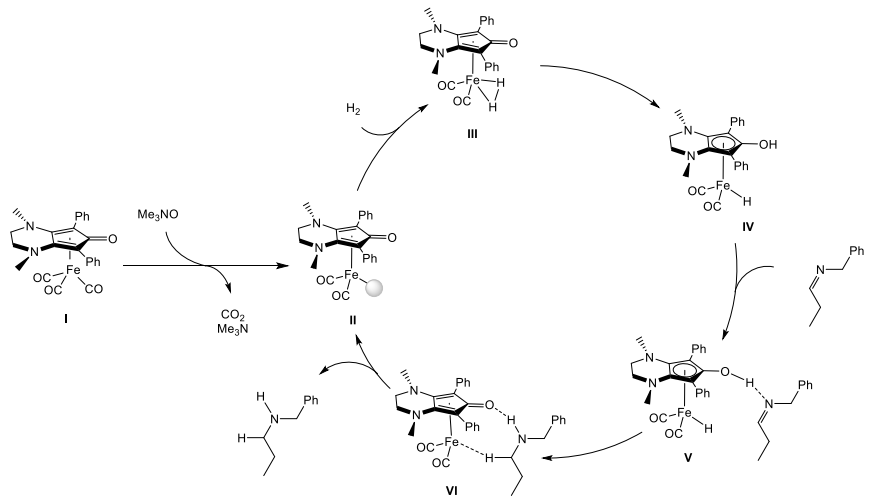
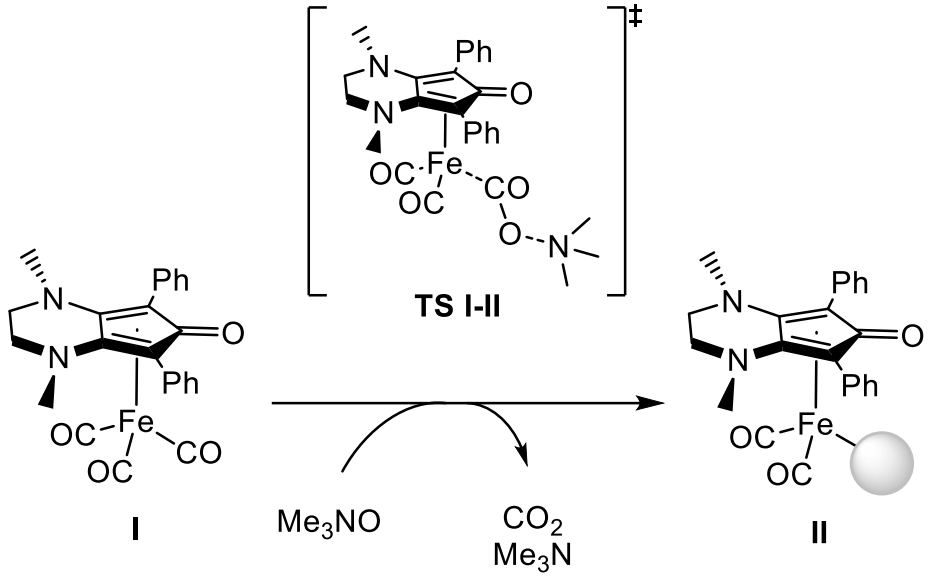


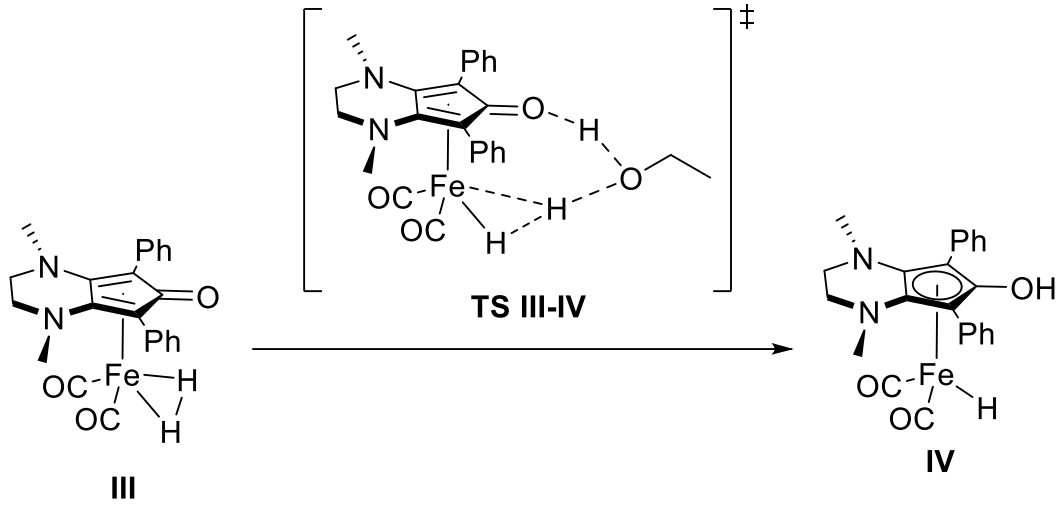
Chem. Eur. J., **2013**, *19*, 17881–17890.

INTRODUCTION

Activation of the catalysts



Hydrogenation of the keto group



OBJECTIVES

Main objectives:

- Investigate the behavior of **different catalyst structures** to identify strategies to **lower activation barriers**, enabling operation under milder conditions that reduce undesired parallel reactions.
- Analyze the results obtained from the modifications made to the catalyst to **understand their impact on catalytic performance**.
- Conduct various tests to **provide a plausible explanation** for the observed results, ensuring a thorough understanding of the catalytic processes involved.

METHODOLOGY

Calculations

- Gaussian 09
- BP86
  - H, C, O, N, F and Si → SVP
  - Fe → SDD

  } Optimization of the geometries

- M06 + PCM
  - H, C, O, N, F and Si → cc-pVTZ
  - Fe → SDD

  } Solvation energy

METHODOLOGY

Complementary studies

- Electronic and geometrical indicators
  - Atomic charges (Natural Population Analysis)
  - Mayer Bond Order (MBO)
  - Fukui function
  - Bond lengths
- Steric maps (SambVca)
- Aromaticity (ESI-3D)

METHODOLOGY

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Atomic charges:
distribution of the electron density in each atom.

Mayer Bond Order (MBO):
average number of electrons shared between two atoms.

Fukui function:
describes the capacity of an atom to deal with an electrophilic attack.

$$f_k = -\left(\frac{\partial q_k}{\partial N}\right)_{\nu(r)} \Longrightarrow f_k = q_k^{N-1} - q_k^N$$

Chem. Phys. Lett., **1983**, *97*, 270–274.
J. Am. Chem. Soc., **1986**, *108*, 5708–5711

METHODOLOGY

Complementary studies

- Electronic and geometrical indicators
  - Atomic charges (Natural Population Analysis)
  - Mayer Bond Order (MBO)
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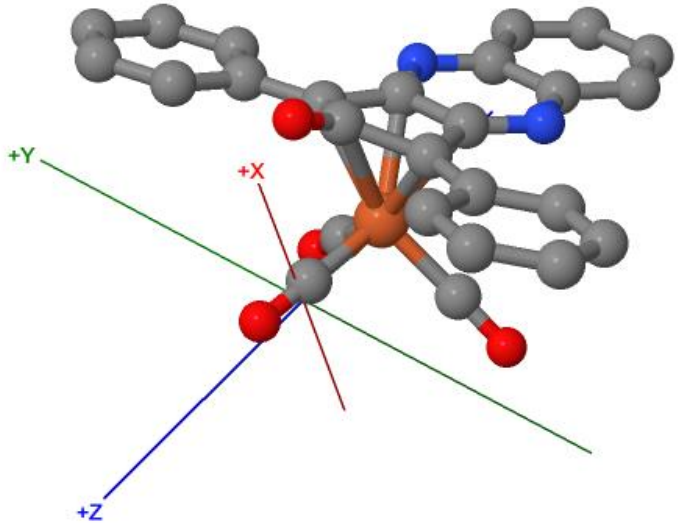
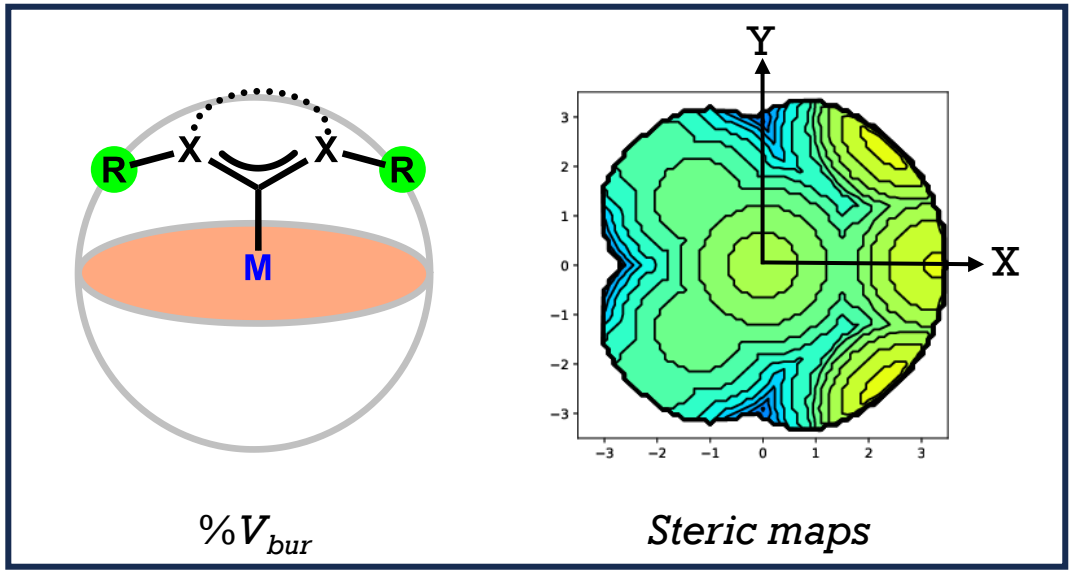
  - Bond lengths
- **Steric maps (SambVca)**
- Aromaticity (ESI-3D)





Nat. Chem., **2019**, *11*, 872–879

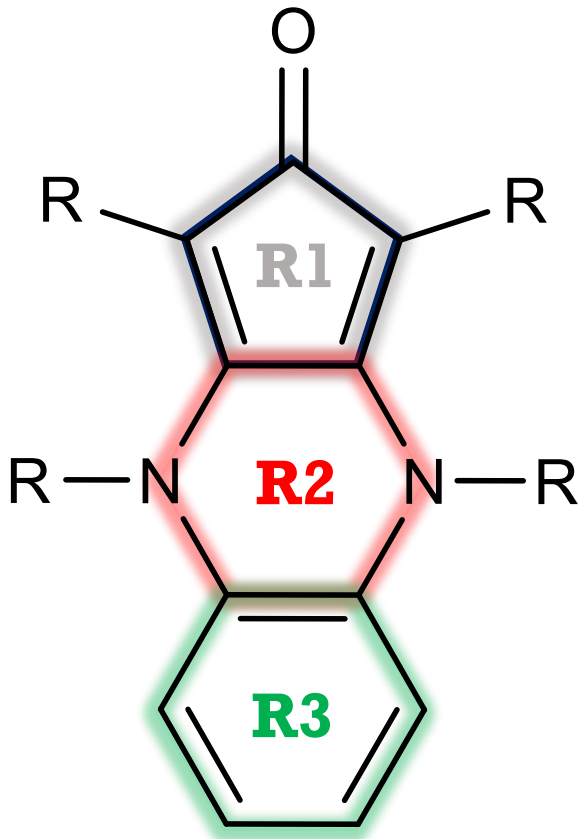
METHODOLOGY

Complementary studies

- Electronic and geometrical indicators
  - Atomic charges (Natural Population Analysis)
  - Mayer Bond Order (MBO)
  - Fukui function
  - Bond lengths
- Steric maps (SambVca)
- Aromaticity (ESI-3D)

Used indices:

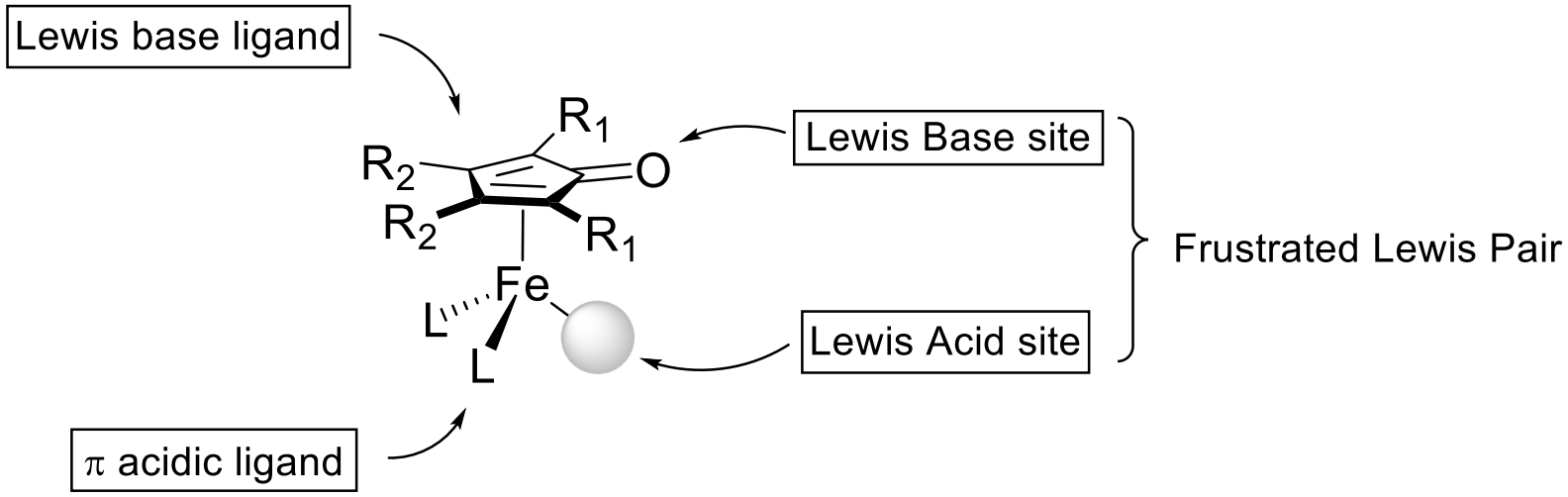
- HOMA
- I_{ring} - I_{NG}
- MCI - I_{NB} ←
- FLU
- BOA
- BLA
- PDI ←



RESULTS AND DISCUSSION

- Examine how the presence of various electron-withdrawing (EWG) and electron-donating (EDG) substituents affects the reactivity and stability of ligands.

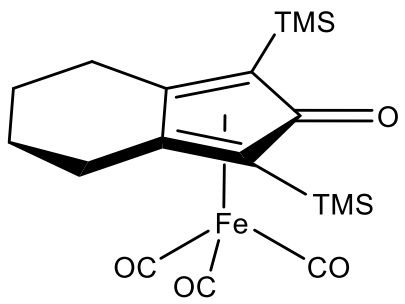
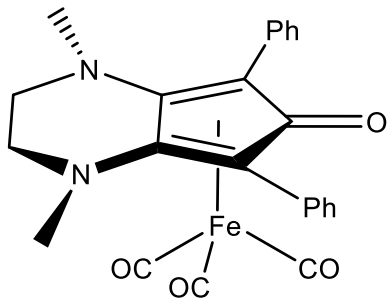
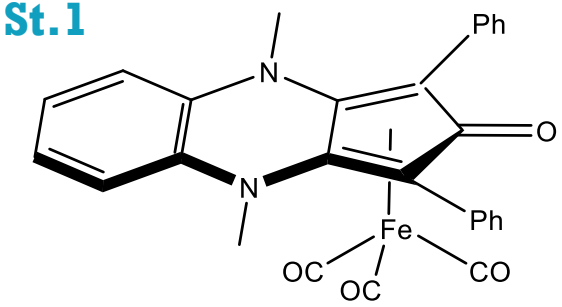
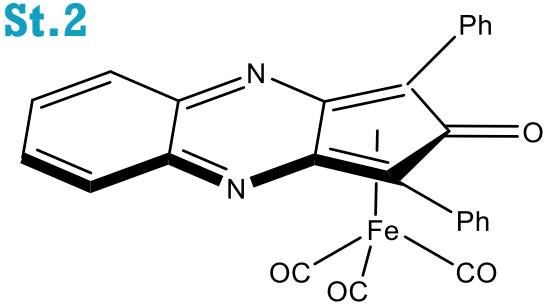
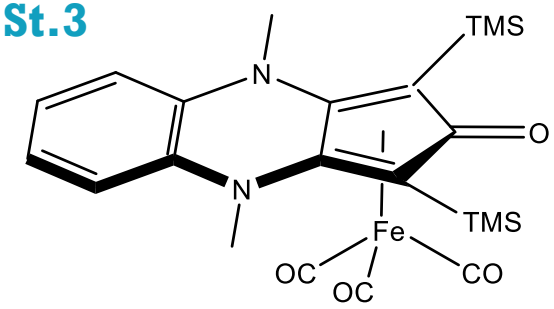
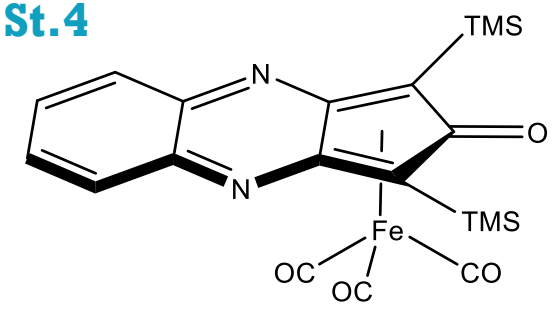
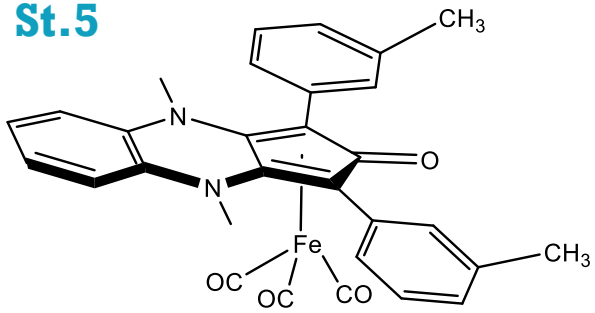
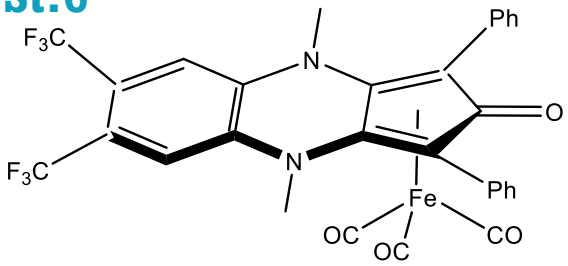
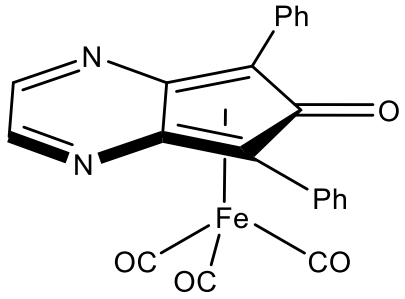
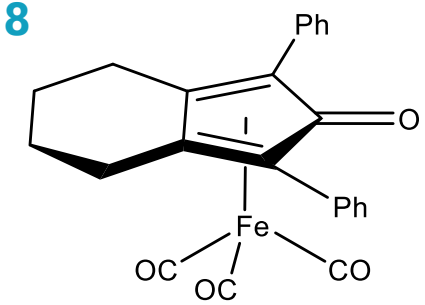
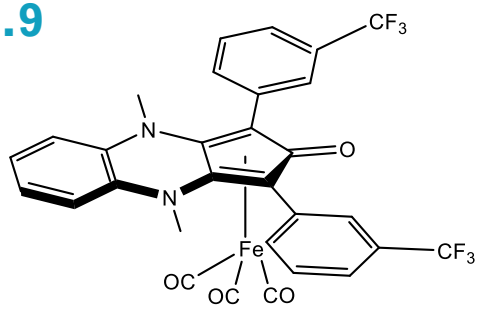
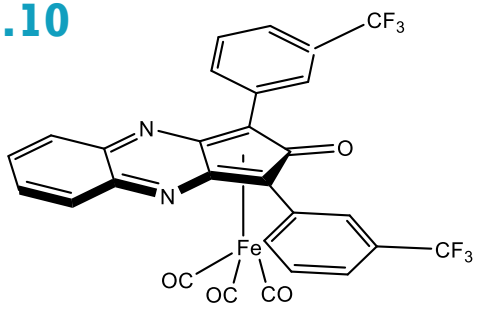
- Introduction of a third annulated ring, aromatic, next to the 6-membered ring also annulated to the 5-membered ring of the cyclopentadienone.



Chin. J. Chem., **2020**, *38*, 1360-1370

RESULTS AND DISCUSSION

[STRUCTURES]

K 	**R** 	**St.1** 	**St.2** 
St.3 	**St.4** 	**St.5** 	**St.6** 
St.7 	**St.8** 	**St.9** 	**St.10** 

RESULTS AND DISCUSSION

[STRUCTURES]

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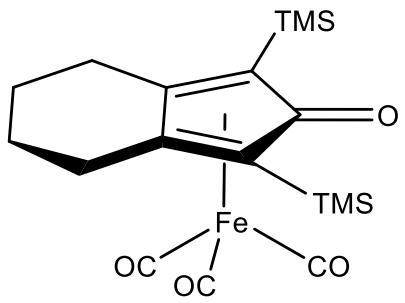

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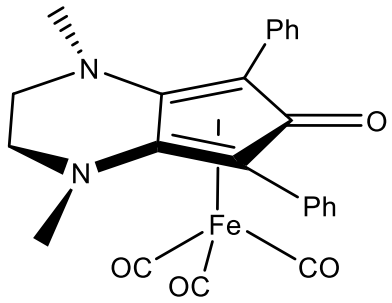
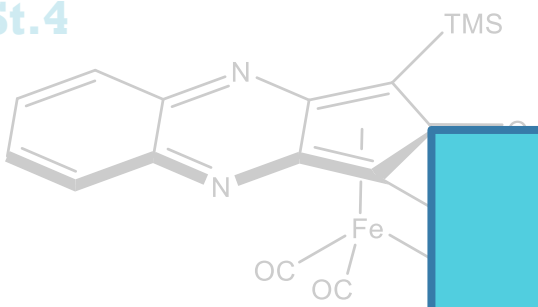


St.1

St.2

St.3

St.4



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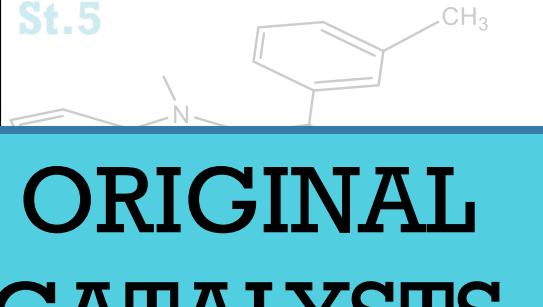
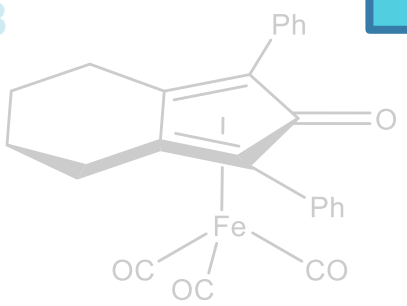


St.6

St.7

St.8



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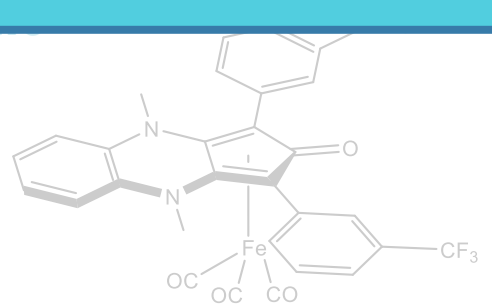


St.10

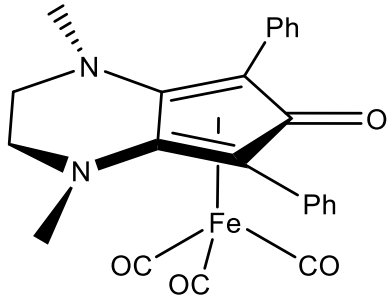
ORIGINAL CATALYSTS

RESULTS AND DISCUSSION

[STRUCTURES]

K

R



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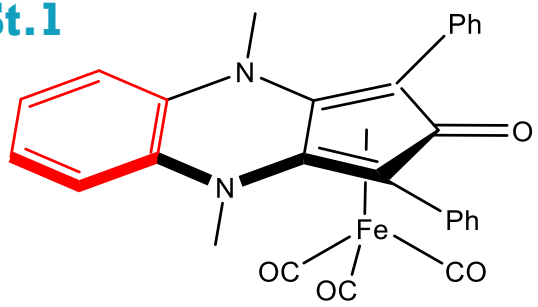

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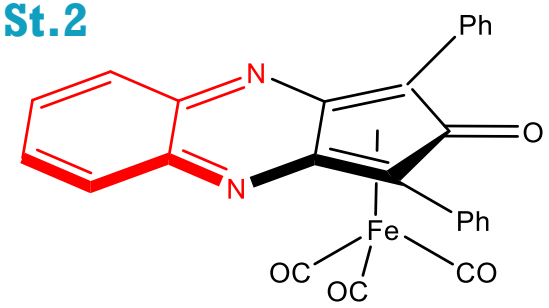

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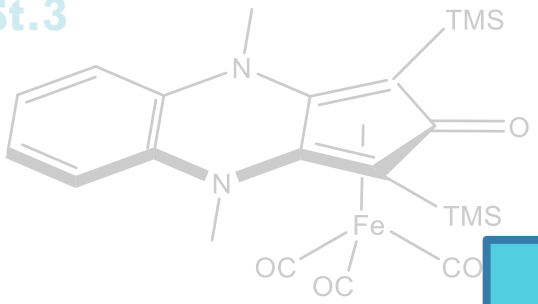

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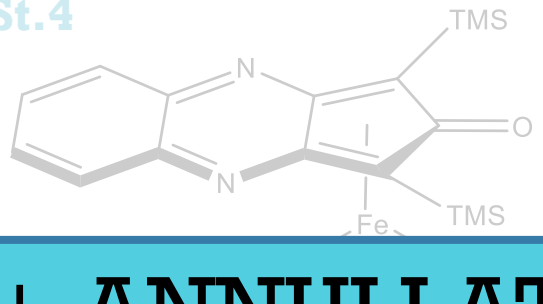

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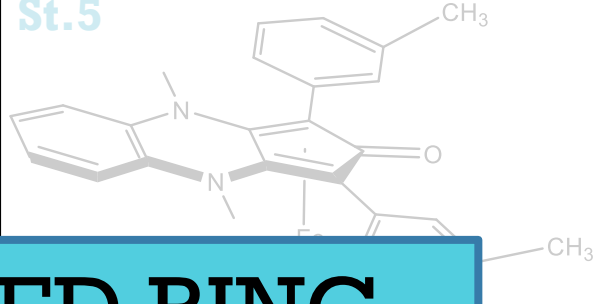


St.6

St.7

St.10

+ ANNULLATED RING

– METHYL

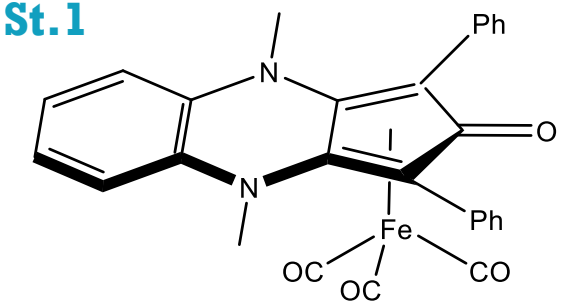
RESULTS AND DISCUSSION

[STRUCTURES]

K

R

St.1



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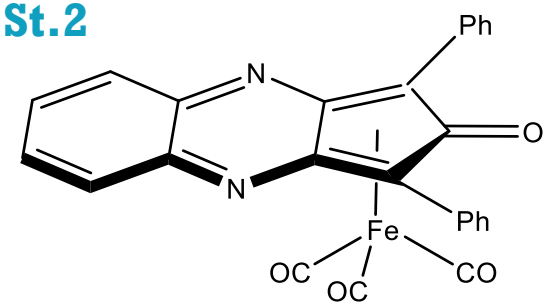
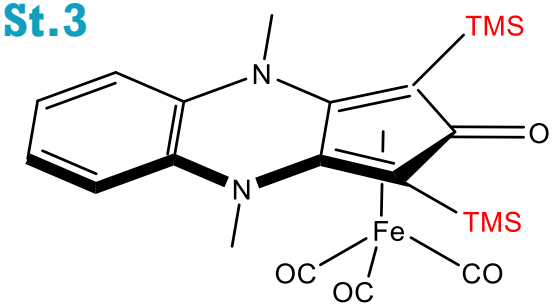


St.3



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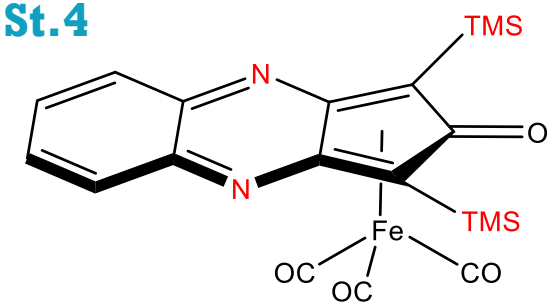

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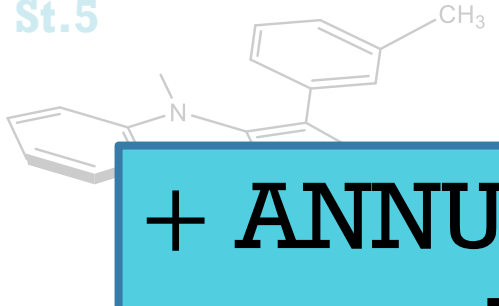

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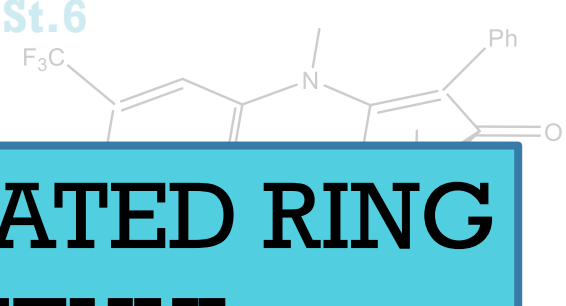
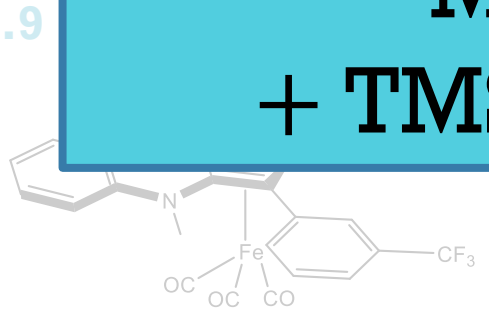
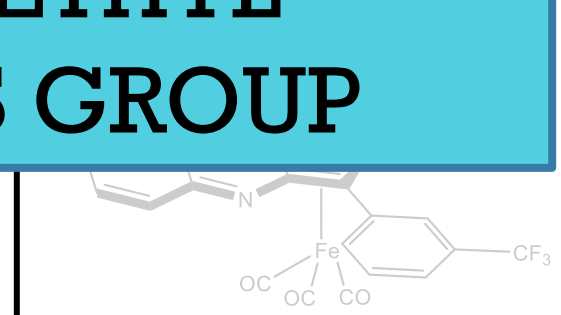


St.7

St.8

St.9





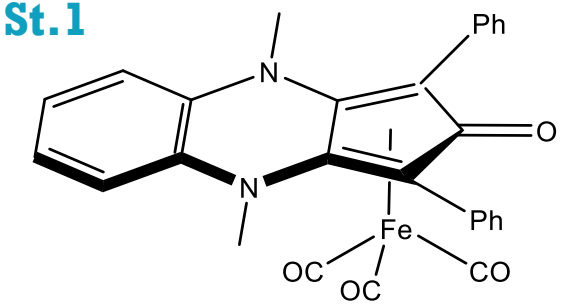
+ ANNULLATED RING
– METHYL
+ TMS GROUP

RESULTS AND DISCUSSION [STRUCTURES]

K

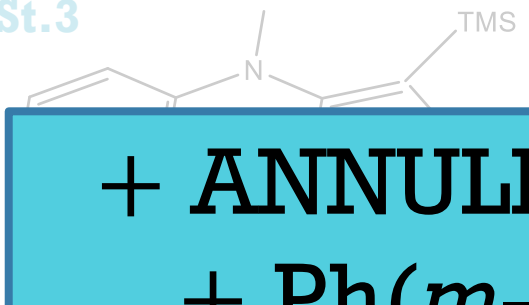
R

St.1

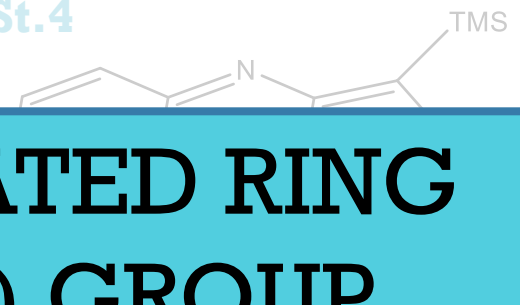


St.2

St.3



St.4



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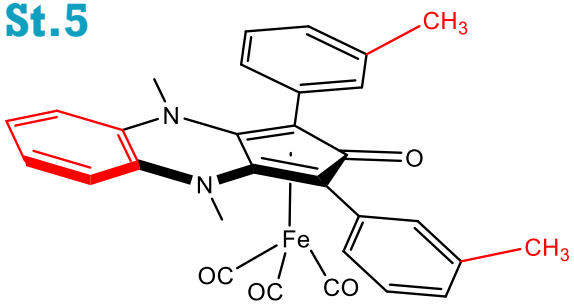

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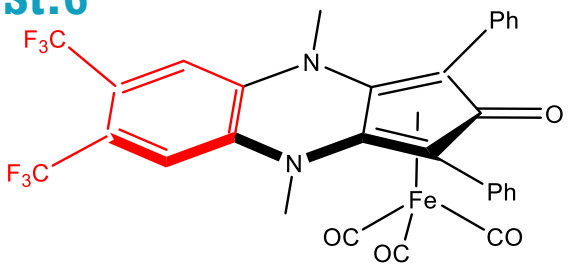

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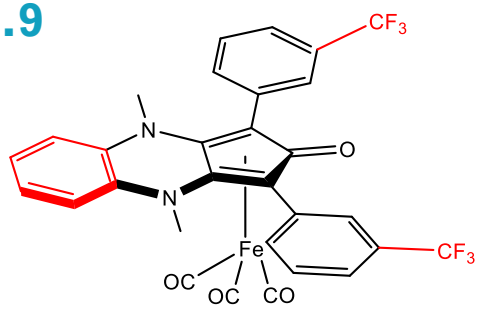

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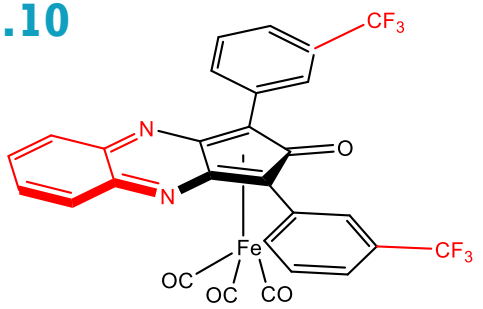
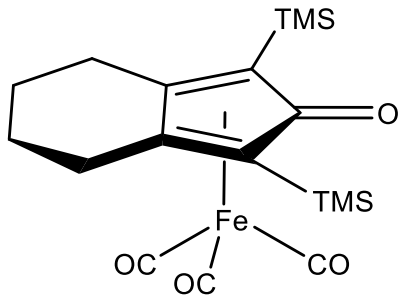


+ ANNULLATED RING
+ Ph(*m*-X) GROUP
+ CF_3 TERMINAL GROUP

RESULTS AND DISCUSSION

[STRUCTURES]

K



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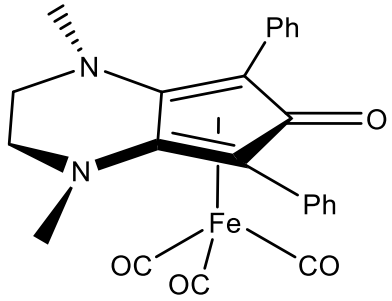


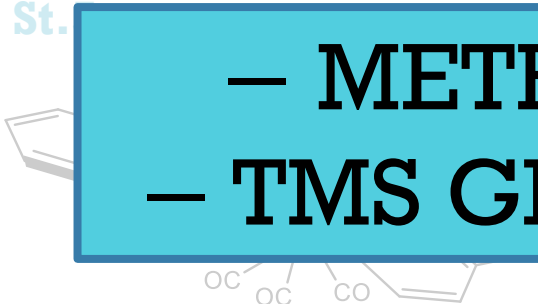
St.1

St.2

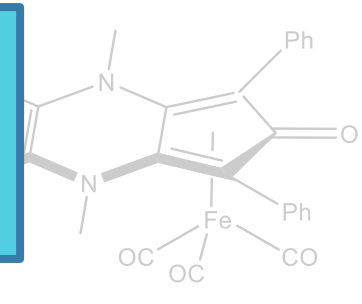
St.3

St.4

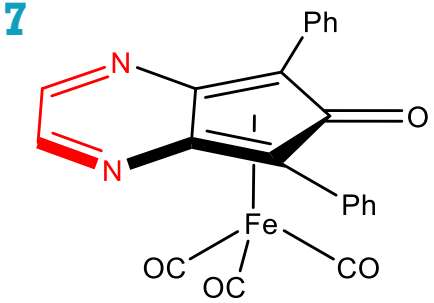
St.



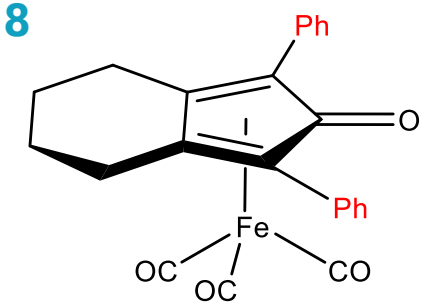
– METHYL
– TMS GROUP



St.7



St.8

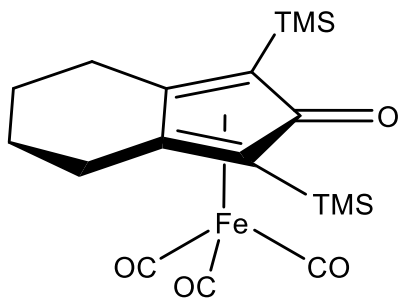
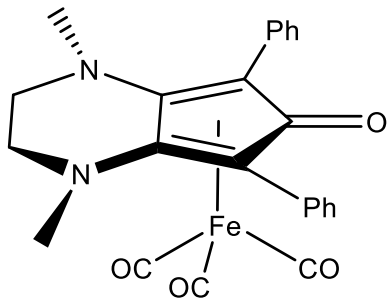
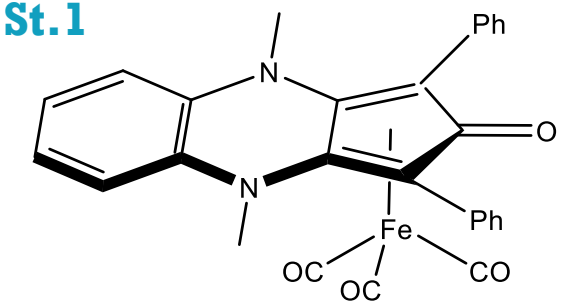
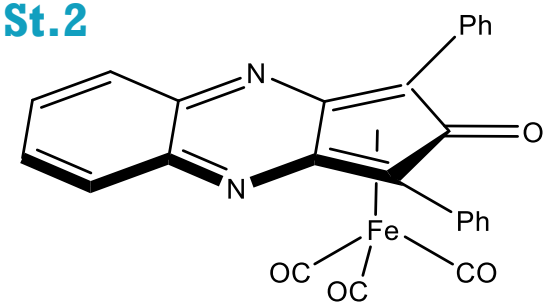
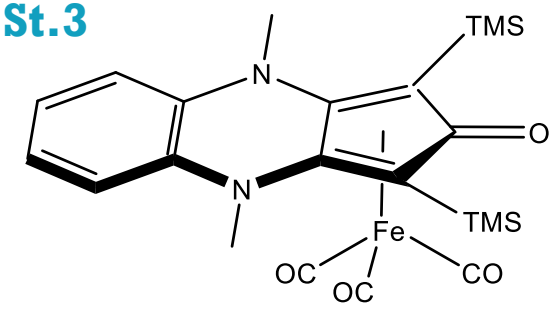
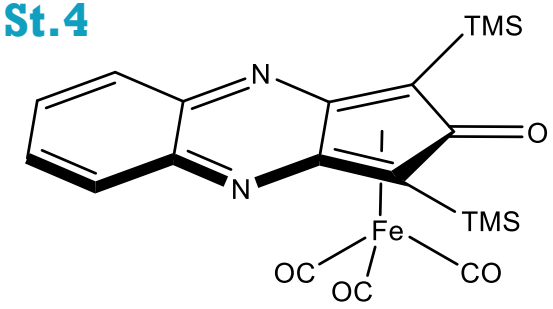
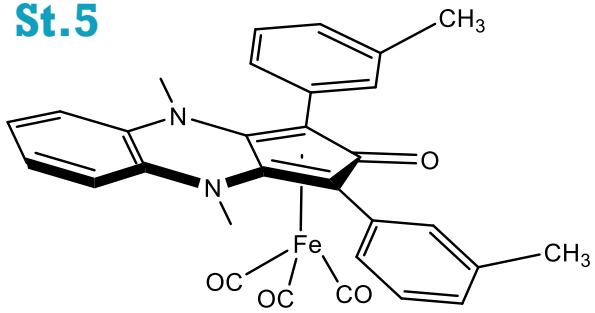
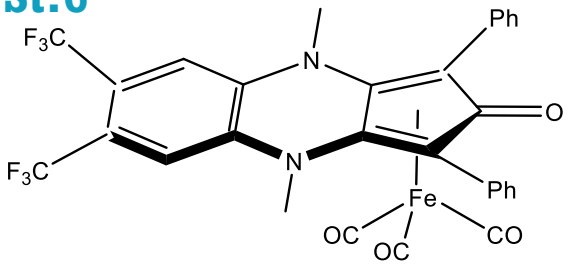
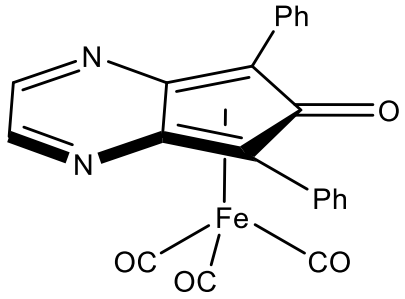
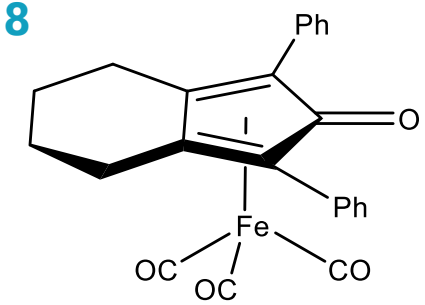
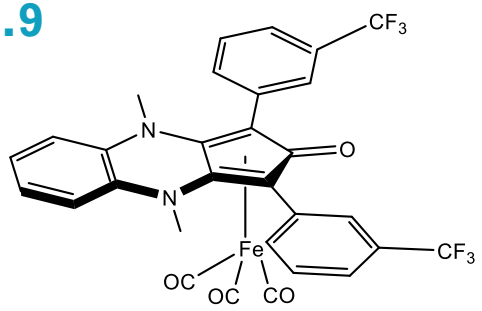
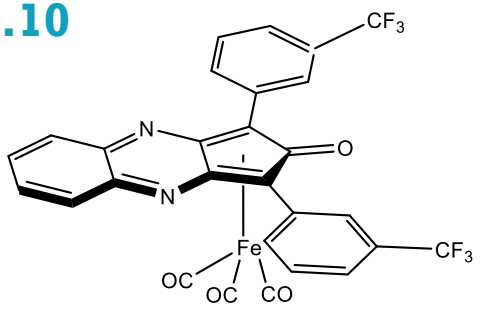


St.9

St.10

RESULTS AND DISCUSSION

[STRUCTURES]

K 	**R** 	**St.1** 	**St.2** 
St.3 	**St.4** 	**St.5** 	**St.6** 
St.7 	**St.8** 	**St.9** 	**St.10** 

RESULTS AND DISCUSSION

[KINETIC COST]

Gibbs energy for studied catalysts (kcal/mol).

	K	R	St.1	St.2	St.3	St.4	St.5	St.6	St.7	St.8	St.9	St.10
I → I-II	18.4	20.6	17.4	9.3	24.2	14.9	18.8	17.8	10.2	15.5	17.2	10.2
III → III-IV	12.5	16.0	13.1	9.8	20.7	11.4	16.2	15.0	11.0	13.9	15.6	10.3

RESULTS AND DISCUSSION

[KINETIC COST]

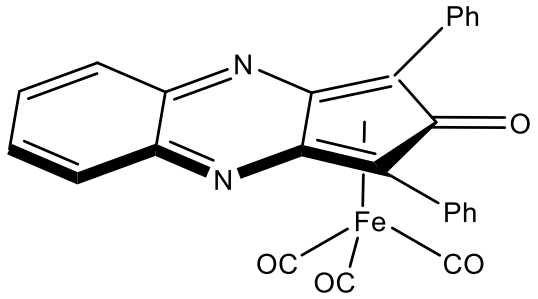
Gibbs energy for studied catalysts (kcal/mol).

	K	R	St.1	St.2	St.3	St.4	St.5	St.6	St.7	St.8	St.9	St.10
I → I-II	18.4	20.6	17.4	9.3	24.2	14.9	18.8	17.8	10.2	15.5	17.2	10.2
III → III-IV	12.5	16.0	13.1	9.8	20.7	11.4	16.2	15.0	11.0	13.9	15.6	10.3

→ values below Renaud's catalyst, more than 3 kcal/mol

→ values below Renaud's catalyst, up to 3 kcal/mol

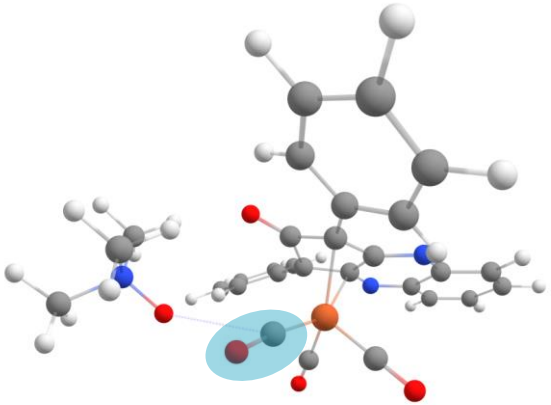
→ values over Renaud's catalyst

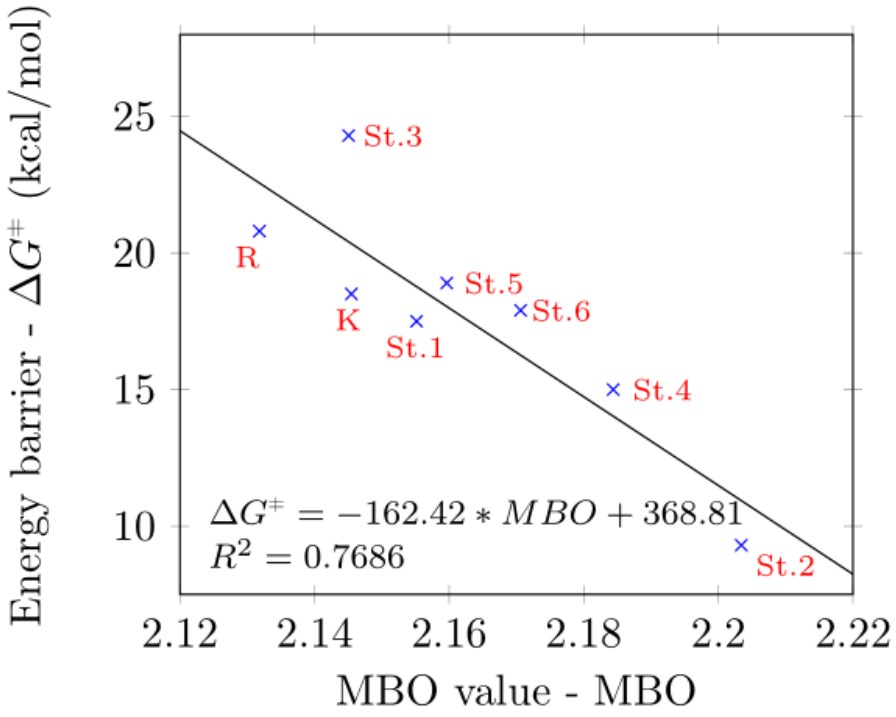


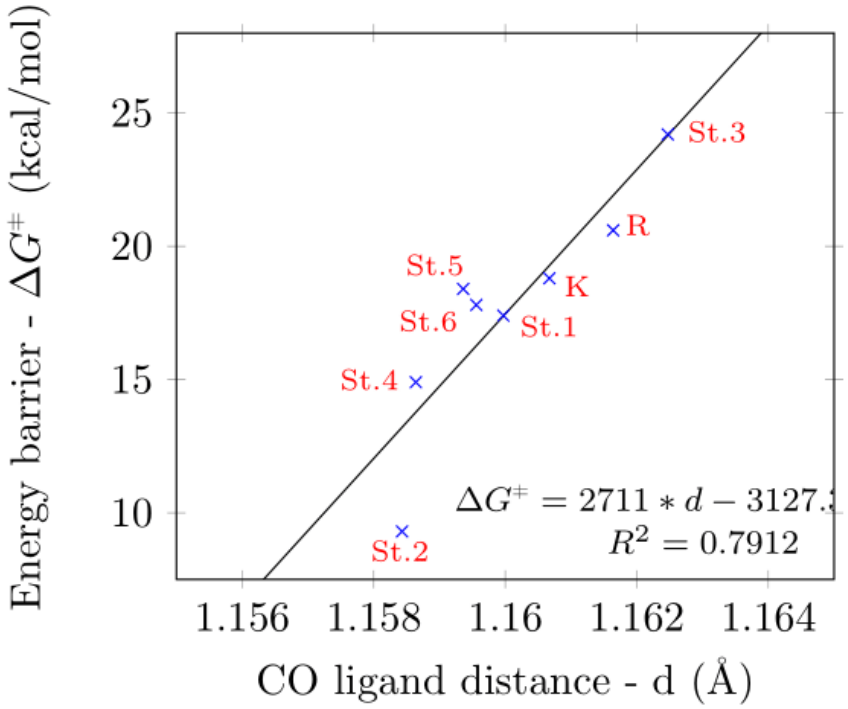
St.2 catalyst

RESULTS AND DISCUSSION

Activation of the catalyst

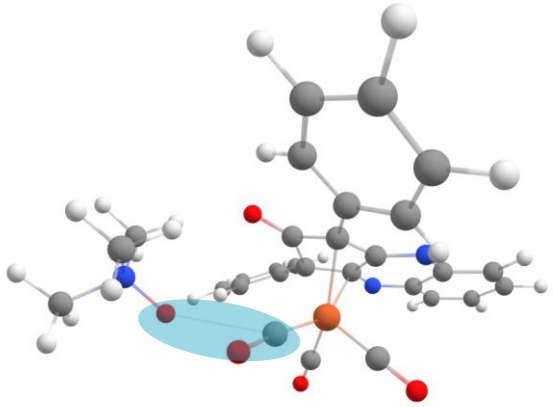






RESULTS AND DISCUSSION

Activation of the catalyst

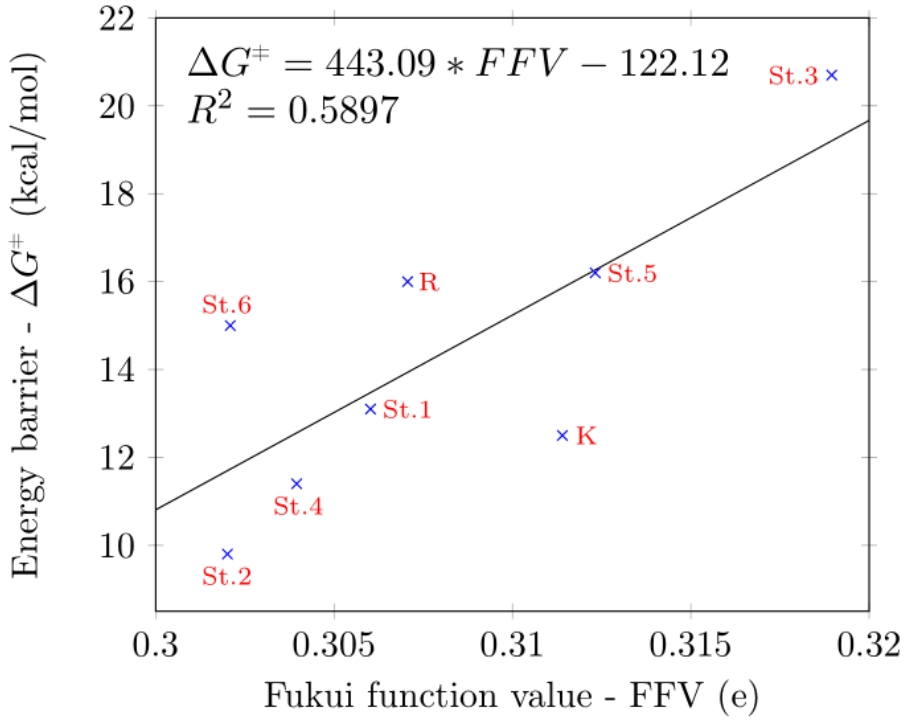


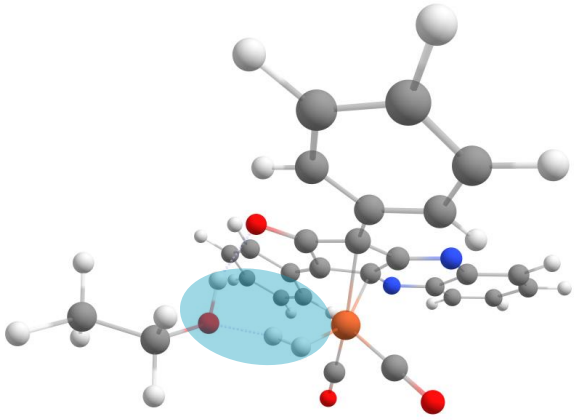
(e)	K	R	St.1	St.2	St.3	St.4	St.5	St.6
qFe	-1.509	-1.528	-1.492	-1.350	-1.502	-1.393	-1.507	-1.510
qC	0.928	0.905	0.903	0.938	0.897	0.946	0.9013	0.905

(Å)			K	R	St.1	St.2	St.3	St.4	St.5	St.6
I	d(Fe−C)		1.795	1.797	1.804	1.775	1.798	1.776	1.806	1.807
	d(C−O)	(ligand)	1.159	1.162	1.160	1.158	1.163	1.159	1.161	1.160
I-II	d(Fe−C)		1.879	1.892	1.885	1.787	1.906	1.845	1.888	1.892
	d(C−O)	(ligand)	1.185	1.188	1.179	1.158	1.194	1.181	1.179	1.180
	d(C−O)	(ligand-Me_3NO)	1.188	1.820	1.954	3.151	1.742	1.947	1.981	1.942

RESULTS AND DISCUSSION

Hydrogen transfer



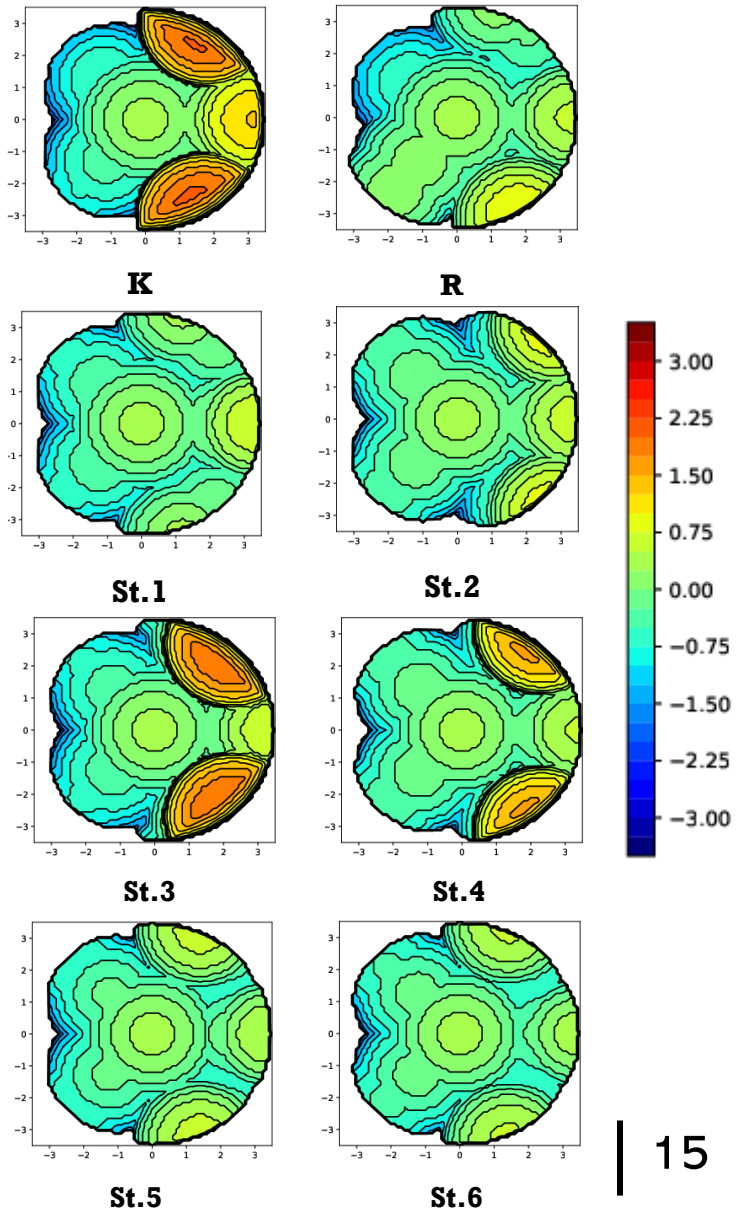


(Å)			K	R	St.1	St.2	St.3	St.4	St.5	St.6
III	**d(Fe−H)**		1.636	1.654	1.663	1.613	1.689	1.613	1.669	1.667
III-IV	**d(Fe−H)**		1.588	1.592	1.620	1.561	1.603	1.563	1.616	1.612
	d(H−O)	(H - EtOH)	1.397	1.350	1.341	1.539	1.328	1.536	1.332	1.348
	d(H−O)	(EtOH - keto)	1.494	1.401	1.412	1.610	1.374	1.569	1.432	1.441

RESULTS AND DISCUSSION

[STERIC MAPS]

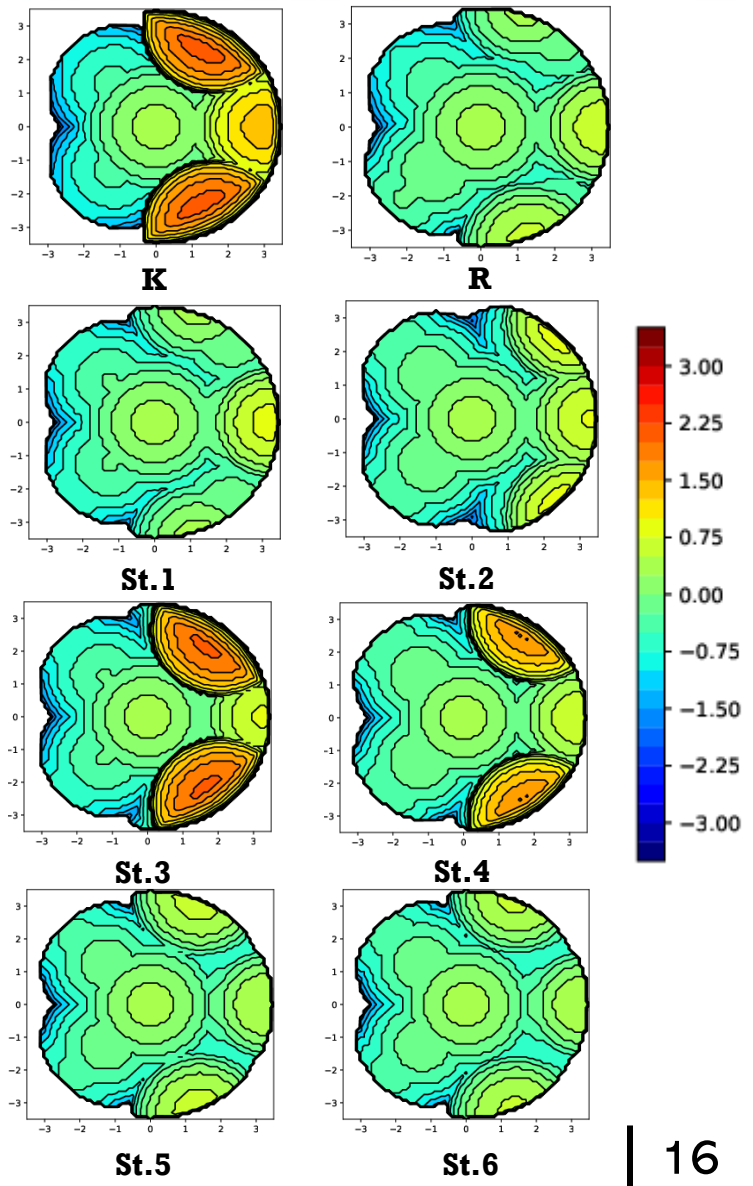
$\%V_{bur}$	I				
	SW	**NW**	**NE**	**SE**	**TOTAL**
K	38.4	36.2	71.1	72.0	54.4
R	47.0	36.3	48.2	56.0	46.9
St.1	39.3	39.3	50.3	50.3	44.8
St.2	41.3	41.4	50.5	50.6	46.0
St.3	38.1	38.1	67.6	67.6	52.8
St.4	41.4	41.4	58.8	58.8	50.1
St.5	40.9	40.8	51.6	51.6	46.2
St.6	41.5	41.2	50.0	50.1	45.7



RESULTS AND DISCUSSION

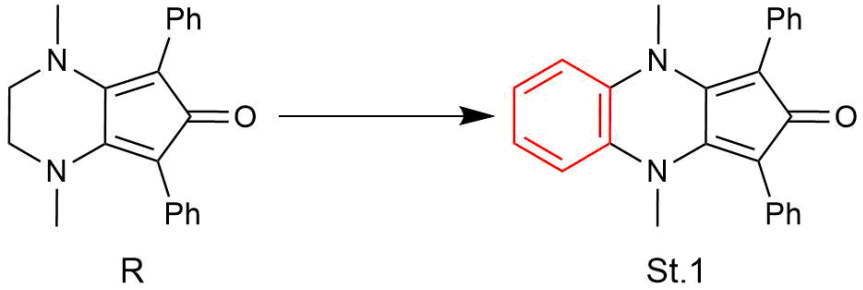
[STERIC MAPS]

$\%V_{bur}$	III				
	SW	NW	NE	SE	TOTAL
K	38.5	38.5	74.1	74.1	56.3
R	43.3	38.9	50.0	52.2	46.1
St.1	39.9	39.9	51.3	51.3	45.6
St.2	41.6	41.6	51.4	51.4	46.5
St.3	39.2	39.1	70.8	70.8	54.9
St.4	41.9	41.9	62.6	62.6	52.3
St.5	41.9	41.9	51.7	51.7	46.8
St.6	42.0	42.2	50.6	50.5	46.3



RESULTS AND DISCUSSION

[AROMATICITY]



Gibbs energy for studied catalysts (kcal/mol).

	K	R	St.1	St.2	St.3	St.4	St.5	St.6	St.7	St.8	St.9	St.10
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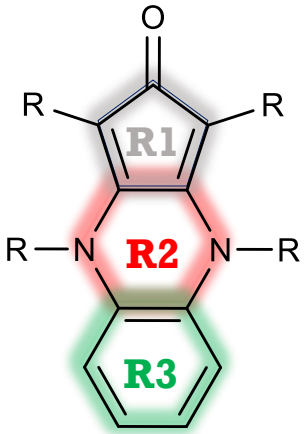
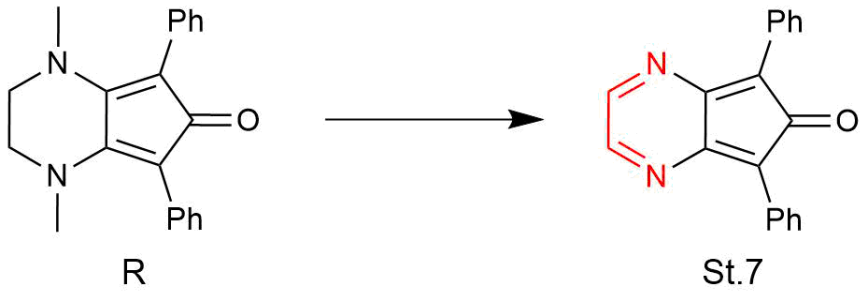


RESULTS AND DISCUSSION

[AROMATICITY]



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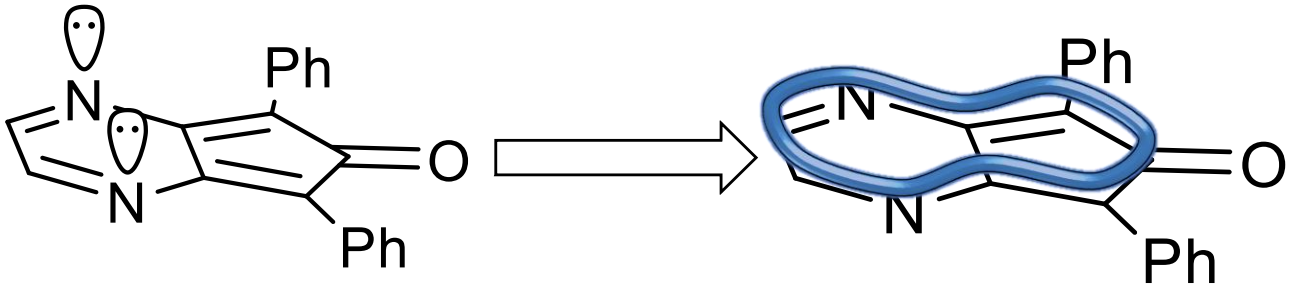
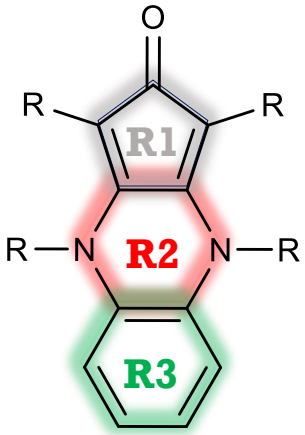
III → III-IV	12.5	16.0	13.1	9.8	20.7	11.4	16.2	15.0	11.0	13.9	15.6	10.3

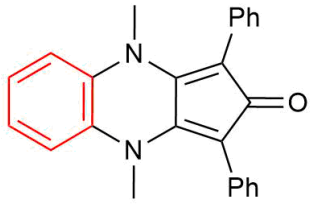
Catalyst	Ring	MCI	I_{ring}	I_{NG}	I_{NB}	FLU	BOA	BLA	PDI	HOMA
R	1	0.0062	0.0076	0.0310	0.0290	0.0770	0.0176	0.0122	–	-1.2788
	2	0.0004	0.0004	0.0184	0.0171	0.0488	0.0893	0.0367	0.0119	-0.6781
St.7	1	0.0059	0.0071	0.0306	0.0287	0.0752	0.0524	0.0156	–	-1.4825
	2	0.0208	0.0159	0.0344	0.0334	0.0374	0.1774	0.0297	0.0642	0.5772



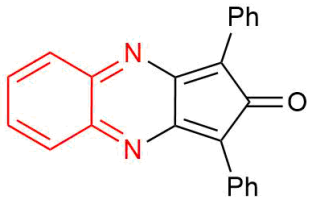


RESULTS AND DISCUSSION

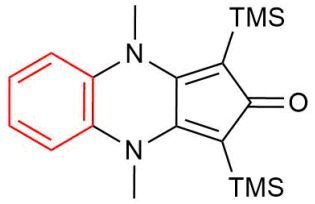
[AROMATICITY]



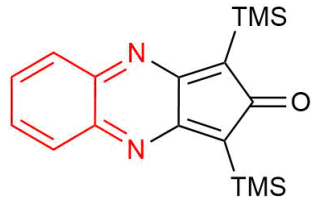
St.1



St.2



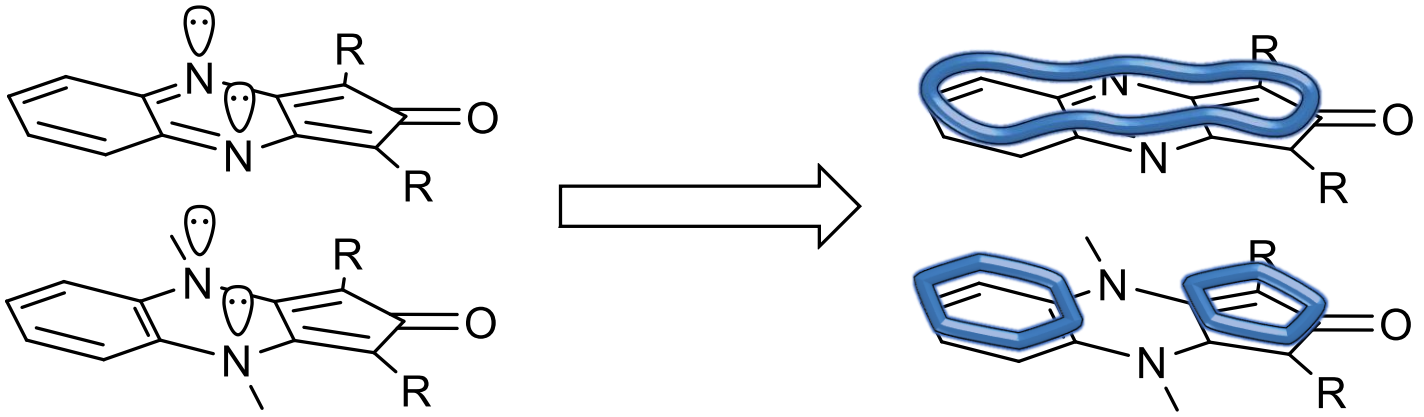
St.3

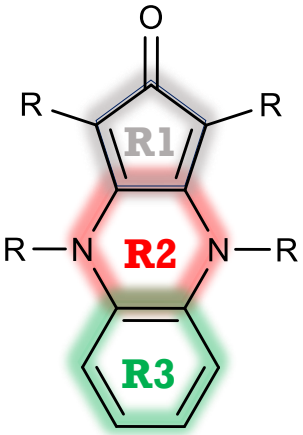


St.4

Gibbs energy for studied catalysts (kcal/mol).

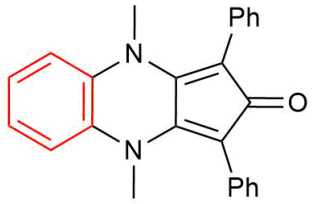
	K	R	St.1	St.2	St.3	St.4
I → I-II	18.4	20.6	17.4	9.3	24.2	14.9
III → III-IV	12.5	16.0	13.1	9.8	20.7	11.4



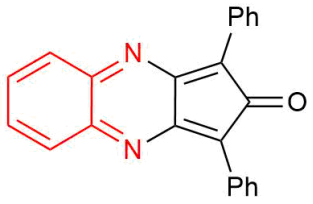


RESULTS AND DISCUSSION

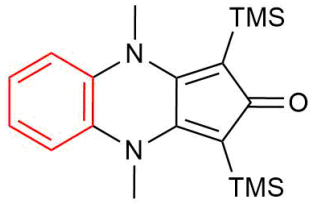
[AROMATICITY]



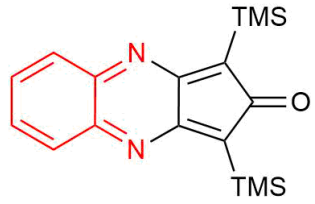
St.1



St.2



St.3

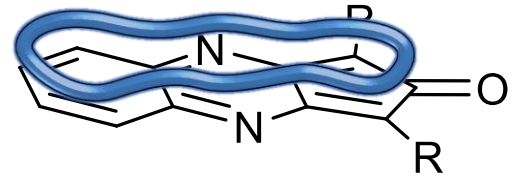


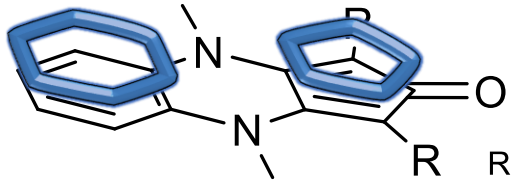
St.4

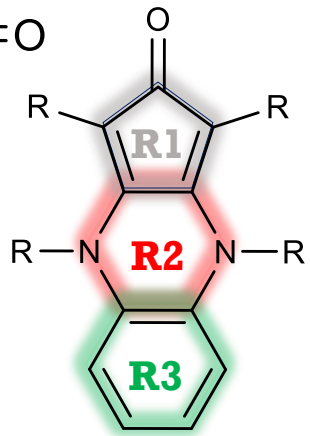
Gibbs energy for studied catalysts (kcal/mol).

	K	R	St.1	St.2	St.3	St.4
I → I-II	18.4	20.6	17.4	9.3	24.2	14.9
III → III-IV	12.5	16.0	13.1	9.8	20.7	11.4

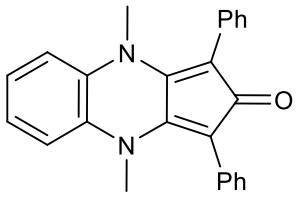
Catalyst	Ring	MCI	I_{ring}	I_{NG}	I_{NB}	FLU	BOA	BLA	PDI	HOMA
St.1	1	0.0066	0.0083	0.0315	0.0294	0.0732	0.0055	0.0097	–	-1.1220
	2	0.0024	0.0020	0.0244	0.0233	0.0272	0.0953	0.0263	0.0164	0.4440
	3	0.0524	0.0358	0.0394	0.0390	0.0036	0.0477	0.0100	0.0864	0.8477
St.2	1	0.0054	0.0065	0.0300	0.0282	0.0794	0.0050	0.0038	–	-1.1220
	2	0.0165	0.0124	0.0330	0.0321	0.0256	0.0477	0.0046	0.0594	0.4440
	3	0.0208	0.0166	0.0346	0.0334	0.0258	0.1991	0.0250	0.0568	0.8477
St.3	1	0.0069	0.0090	0.0321	0.0296	0.0558	0.0097	0.0086	–	-1.1802
	2	0.0024	0.0020	0.0243	0.0233	0.0285	0.0890	0.0253	0.0169	0.4325
	3	0.0523	0.0358	0.0393	0.0390	0.0036	0.0481	0.0097	0.0864	0.8534
St.4	1	0.0056	0.0072	0.0307	0.0284	0.0638	0.0205	0.0008	–	-1.5009
	2	0.0166	0.0125	0.0330	0.0322	0.0272	0.0551	0.0046	0.0595	0.2862
	3	0.0207	0.0165	0.0346	0.0334	0.0261	0.2006	0.0243	0.0567	0.3614



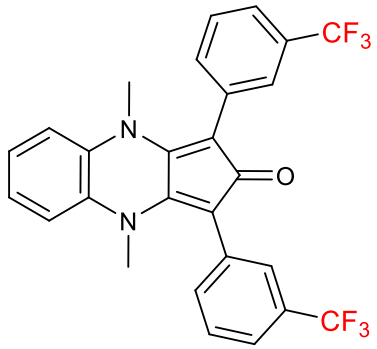




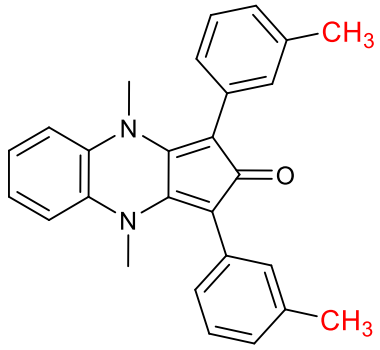
RESULTS AND DISCUSSION



St.1



St.9

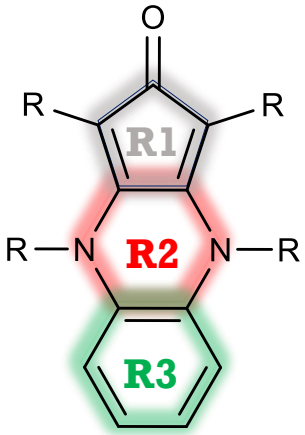


St.5

Gibbs energy for studied catalysts (kcal/mol).

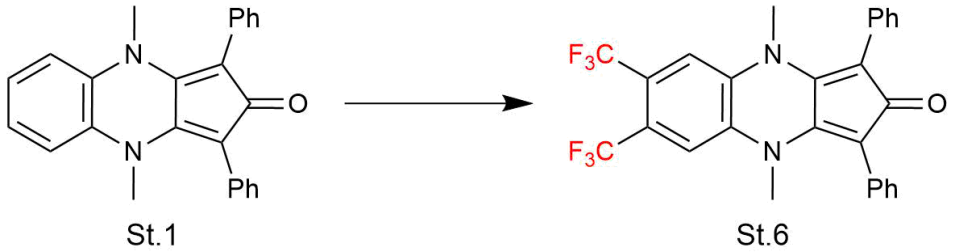
	K	R	St.1	St.2	St.3	St.4	St.5	St.6	St.7	St.8	St.9	St.10
I → I-II	18.4	20.6	17.4	9.3	24.2	14.9	18.8	17.8	10.2	15.5	17.2	10.2
III → III-IV	12.5	16.0	13.1	9.8	20.7	11.4	16.2	15.0	11.0	13.9	15.6	10.3

Catalyst	Ring	MCI	I_{ring}	I_{NG}	I_{NB}	FLU	BOA	BLA	PDI	HOMA
St.1	1	0.0066	0.0083	0.0315	0.0294	0.0732	0.0055	0.0097	–	-1.1220
	2	0.0024	0.0020	0.0244	0.0233	0.0272	0.0953	0.0263	0.0164	0.4440
	3	0.0524	0.0358	0.0394	0.0390	0.0036	0.0477	0.0100	0.0864	0.8477
St.9	1	0.0066	0.0082	0.0315	0.0293	0.0735	0.0599	0.0076	–	-1.1087
	2	0.0024	0.0020	0.0244	0.0234	0.0272	0.1003	0.0282	0.0165	0.4419
	3	0.0526	0.0360	0.0394	0.0390	0.0036	0.0465	0.0098	0.0867	0.8504
St.5	1	0.0066	0.0083	0.0315	0.0293	0.0741	0.0093	0.0089	–	-1.0785
	2	0.0024	0.0021	0.0245	0.0234	0.0264	0.0923	0.0275	0.0138	0.4380
	3	0.0521	0.0357	0.0393	0.0389	0.0036	0.0460	0.0098	0.0860	0.8413



RESULTS AND DISCUSSION

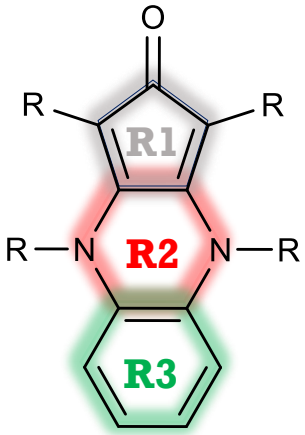
[AROMATICITY]



Gibbs energy for studied catalysts (kcal/mol).

	K	R	St.1	St.2	St.3	St.4	St.5	St.6	St.7	St.8	St.9	St.10
I → I-II	18.4	20.6	17.4	9.3	24.2	14.9	18.8	17.8	10.2	15.5	17.2	10.2
III → III-IV	12.5	16.0	13.1	9.8	20.7	11.4	16.2	15.0	11.0	13.9	15.6	10.3

Catalyst	Ring	MCI	I_{ring}	I_{NG}	I_{NB}	FLU	BOA	BLA	PDI	HOMA
St.1	1	0.0066	0.0083	0.0315	0.0294	0.0732	0.0055	0.0097	–	-1.1220
	2	0.0024	0.0020	0.0244	0.0233	0.0272	0.0953	0.0263	0.0164	0.4440
	3	0.0524	0.0358	0.0394	0.0390	0.0036	0.0477	0.0100	0.0864	0.8477
St.6	1	0.0066	0.0083	0.0315	0.0293	0.0749	0.0121	0.0099	–	-1.1371
	2	0.0026	0.0022	0.0248	0.0236	0.0255	0.0588	0.0186	0.0137	0.4855
	3	0.0444	0.0310	0.0384	0.0379	0.0050	0.0332	0.0077	0.0766	0.8312



CONCLUSIONS

1. Explored **the potential of modified Knölker-type iron complexes** as catalysts for catalytic hydrogenation.

2. Computational analyses revealed that altering the substituents on the cyclopentadienone structure **significantly reduces energy barriers**, enhancing reactivity.

3. Advanced computational techniques provided a **detailed understanding** of the electronic and geometric properties of the catalysts.

4. **Demonstrated that careful structural modifications can lead to the development of more efficient and sustainable catalysts.**

Modifying catalytic sustainability: aromaticity, conceptual DFT and steric mapping

Carles Alcaide i Blaya

Supervisors:

Dr. Albert Poater Teixidor

Dra. Sílvia Simon Rabaseda

diMOcat

Universitat de Girona
Facultat de Ciències

[Supplementary material]

Modifying catalytic sustainability: aromaticity, conceptual DFT and steric mapping

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Correlacions del índexs d'aromaticitat pel compostos I i III (St.1 a St.6)

	MCI	*Iring*	*I_NG*	*I_NB*	*FLU*	*BOA*	*BLA*	*PDI*	*HOMA*
MCI	1								
Iring	0,99092	1							
I_NG	0,813111	0,875709	1						
I_NB	0,861008	0,910597	0,99423	1					
FLU	-0,719329	-0,657272	-0,441387	-0,522308	1				
BOA	0,042001	0,007665	-0,050811	-0,01131	-0,435547	1			
BLA	-0,250379	-0,315462	-0,505525	-0,464894	-0,250509	0,70784	1		
PDI	0,949827	0,961322	0,972424	0,973618	-0,730348	-0,122839	-0,626943	1	
HOMA	0,574338	0,533514	0,452668	0,515381	-0,896696	0,408549	0,311603	0,488149	1

Correlacions del índexs d'aromaticitat pel compostos I-II i III-IV (St.1 a St.6)

	MCI	*Iring*	*I_NG*	*I_NB*	*FLU*	*BOA*	*BLA*	*PDI*	*HOMA*
MCI	1								
Iring	0,986202	1							
I_NG	0,784385	0,865403	1						
I_NB	0,829496	0,896371	0,995162	1					
FLU	-0,732986	-0,669458	-0,471439	-0,539769	1				
BOA	0,113556	0,088357	0,057337	0,080886	-0,240826	1			
BLA	-0,099673	-0,171047	-0,380705	-0,352452	-0,10996	0,668696	1		
PDI	0,952797	0,963255	0,96971	0,968167	-0,734278	0,069282	-0,432981	1	
HOMA	0,556871	0,516436	0,47015	0,521191	-0,891266	0,222036	0,106725	0,494006	1

Catalyst	Ring	MCI	I_{ring}	I_{NG}	I_{NB}	FLU	BOA	BLA	PDI	HOMA
K I-II	1	0,009747	0,011851	0,033874	0,03171	0,042374	0,02546	0,013623	–	-0,942953
	2	0,000338	0,000348	0,018174	0,016811	0,08011	0,05388	0,01389	0,011426	-3,503055
K III-IV	1	0,011739	0,013929	0,034987	0,032912	0,033566	0,02424	0,001689	–	-0,505022
	2	0,000336	0,000347	0,018172	0,016792	0,079761	0,053996	0,013483	0,011583	-3,476028
R I-II	1	0,007244	0,008892	0,031983	0,029882	0,065658	0,024784	0,004108	–	-0,909326
	2	0,000273	0,000367	0,018343	0,016225	0,04771	0,043717	0,02234	0,012746	-0,730832
R III-IV	1	0,008893	0,01061	0,033133	0,031134	0,054225	0,032758	0,004649	–	-0,542367
	2	0,000299	0,000376	0,018411	0,016469	0,047723	0,053427	0,025807	0,012679	-0,737181

Catalyst	Ring	MCI	I_{ring}	I_{NG}	I_{NB}	FLU	BOA	BLA	PDI	HOMA
St.1 I-II	1	0,007536	0,009316	0,032283	0,03012	0,064853	0,02978	0,004779	–	-0,806461
	2	0,002249	0,001868	0,024052	0,023055	0,027398	0,067395	0,017033	0,016307	0,456618
	3	0,051495	0,035315	0,039258	0,038851	0,003801	0,053582	0,011073	0,085634	0,838039
St.1 III-IV	1	0,009348	0,011157	0,033468	0,031447	0,053268	0,041494	0,008406	–	-0,419831
	2	0,002297	0,001946	0,024217	0,023137	0,026544	0,06894	0,019668	0,01374	0,492405
	3	0,051589	0,035385	0,039271	0,038863	0,003699	0,046348	0,010247	0,085513	0,832797

Catalyst	Ring	MCI	I_{ring}	I_{NG}	I_{NB}	FLU	BOA	BLA	PDI	HOMA
St.2 I-II	1	0,005898	0,00698	0,030471	0,028679	0,077076	0,047335	0,012809	–	-1,392426
	2	0,016326	0,012335	0,032945	0,032081	0,025692	0,048622	0,004052	0,058865	0,382203
	3	0,020998	0,016717	0,034657	0,033456	0,025497	0,196298	0,023379	0,056902	0,398493
St.2 III-IV	1	0,006965	0,008275	0,031526	0,029649	0,064283	0,024724	0,001122	–	-0,984515
	2	0,016978	0,012752	0,033128	0,032291	0,024869	0,035412	0,001564	0,059832	0,385355
	3	0,022009	0,017317	0,034862	0,033719	0,024671	0,194025	0,023945	0,057937	0,418035

Catalyst	Ring	MCI	I_{ring}	I_{NG}	I_{NB}	FLU	BOA	BLA	PDI	HOMA
St.3 I-II	1	0,008443	0,010590	0,033120	0,030812	0,047764	0,026237	0,003400	–	-1,001857
	2	0,002105	0,001780	0,023860	0,022802	0,028223	0,049285	0,014471	0,014038	0,459270
	3	0,051162	0,035114	0,039221	0,038809	0,003755	0,047702	0,009447	0,085133	0,840830
St.3 III-IV	1	0,009921	0,012227	0,034086	0,031822	0,038790	0,040573	0,000855	–	-0,525112
	2	0,002310	0,001968	0,024264	0,023158	0,027330	0,065152	0,018512	0,013948	0,461141
	3	0,051313	0,035226	0,039242	0,038828	0,003729	0,044115	0,009051	0,085332	0,839934

Catalyst	Ring	MCI	I_{ring}	I_{NG}	I_{NB}	FLU	BOA	BLA	PDI	HOMA
St.4 I-II	1	0,006293	0,007971	0,031291	0,029053	0,059421	0,034395	0,001776	–	-1,359512
	2	0,017067	0,012734	0,033121	0,032320	0,024932	0,024826	0,000839	0,059395	0,337254
	3	0,023741	0,018320	0,035190	0,034147	0,023074	0,185957	0,022433	0,059619	0,424610
St.4 III-IV	1	0,007583	0,009397	0,032338	0,030157	0,050539	0,043357	0,004181	–	-0,921155
	2	0,017162	0,012846	0,033169	0,032350	0,025704	0,038864	0,001455	0,059960	0,340818
	3	0,022267	0,017445	0,034905	0,033784	0,024517	0,193205	0,023228	0,058220	0,398764

Catalyst	Ring	MCI	I_{ring}	I_{NG}	I_{NB}	FLU	BOA	BLA	PDI	HOMA
St.5 I-II	1	0,007471	0,009245	0,032233	0,030067	0,065685	0,012375	0,001685	–	-0,777744
	2	0,002238	0,001895	0,024110	0,023036	0,026889	0,064262	0,018236	0,013438	0,472640
	3	0,051116	0,035105	0,039219	0,038803	0,003774	0,049831	0,010608	0,085092	0,830616
St.5 III-IV	1	0,009043	0,010879	0,033299	0,031238	0,054179	0,004143	0,005819	–	-0,418301
	2	0,002297	0,001943	0,024212	0,023137	0,026454	0,067917	0,019549	0,013405	0,476666
	3	0,051391	0,035271	0,039250	0,038838	0,003721	0,047114	0,010268	0,085333	0,831365

Catalyst	Ring	MCI	I_{ring}	I_{NG}	I_{NB}	FLU	BOA	BLA	PDI	HOMA
St.6 I-II	1	0,007647	0,009407	0,032345	0,030208	0,065448	0,046147	0,021952	–	-0,814199
	2	0,002319	0,001993	0,024313	0,023174	0,026426	0,030672	0,009056	0,013603	0,505645
	3	0,042939	0,030058	0,038218	0,037692	0,005337	0,035370	0,008136	0,074833	0,818369
St.6 III-IV	1	0,009414	0,011215	0,033503	0,031490	0,053684	0,020758	0,011606	–	-0,437773
	2	0,002396	0,002056	0,024440	0,023300	0,025975	0,035604	0,010827	0,013845	0,525521
	3	0,043578	0,030445	0,038299	0,037785	0,005202	0,033168	0,007922	0,075586	0,820731