Scaled Hypersphere Search Method for Mapping All Reaction Pathways on Potential Energy Surface

Development of a New Algorithm

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This is **Ptolemaios's map**, in which *JAPAN* and *AMERICA* are *missing*!

To know the World entirely,

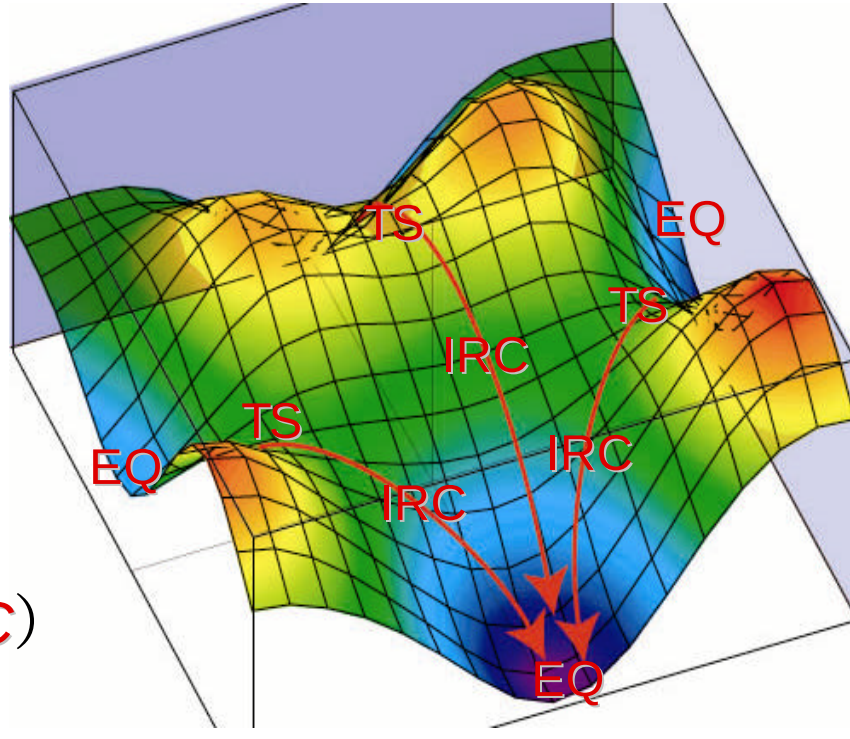
Global Mapping is necessary.

Discovery of New Routes

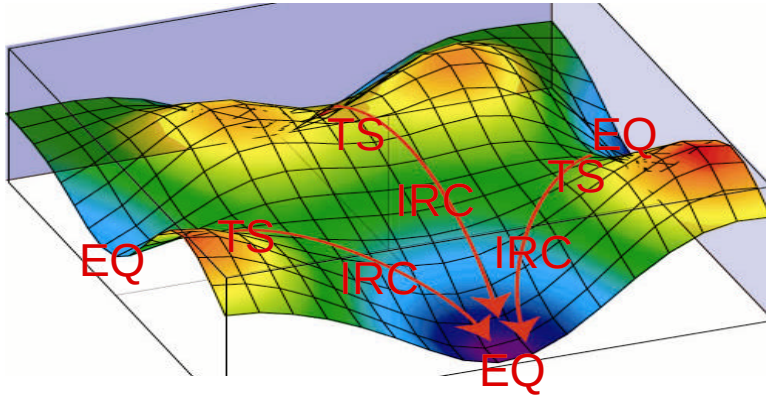
1492 Christpher Columbus
1498 Vasco da Gama
1497 Sebastien Gabbot
1499 Amerigo Vespucci
1519 Ferdinand Magellan

To know the World of Stereo Dynamics in detail, Global Mapping of Potential Energy Surfaces (PES) is important.

- Minima：
  Equilibrium Structures (*EQ*)
- Saddle points:
  Transition States (*TS*)
- Valleys:
  Intrinsic Reaction Coordinates (*IRC*)



Algorithms for PES Mapping



- *EQ*: Geometry Optimization

  Problem Depend on the initial guess!

- *TS*:

  SEAM : Jensen (1992)

  αBB : Floudas et al. (1992)

  Eigen Vector Following (*EVF*) : Cerjan & Miller (1981)

  Gradient Extremal (*GE*) : Sun & Ruedenberg (1993)

  Sphere Optimization (*SO*) : Abashkin & Russo (1994)

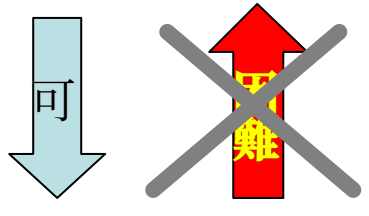
  Nudged Elastic Band (*NEB*) : Jonsson et al. (1998)

  Problem Partially possible, but generally impossible!

- *IRC*:

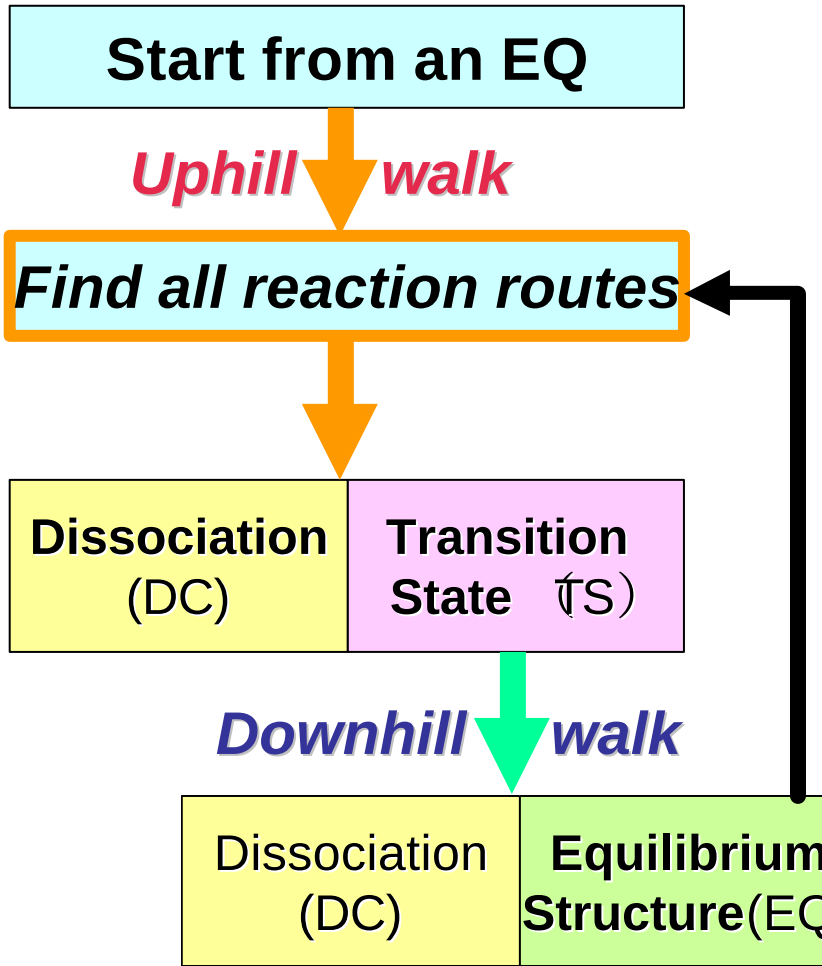
  Downhill walks are possible by Steepest Descent Method.

  Problem *Uphill walks are impossible!*

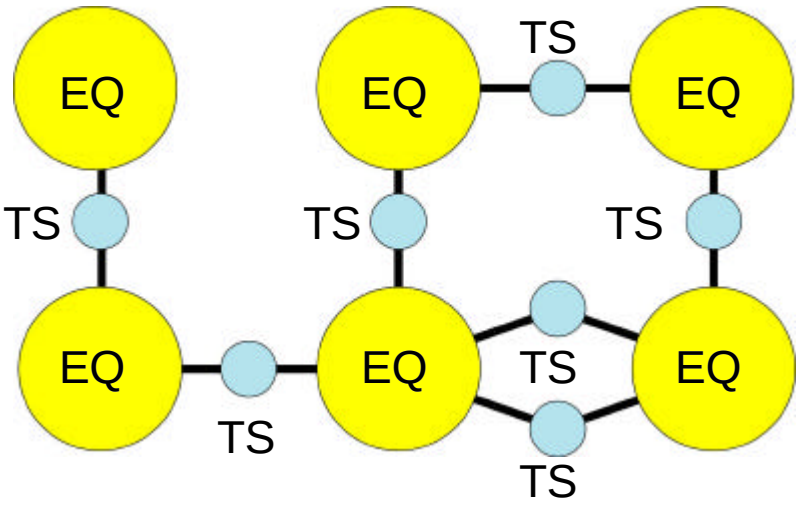


A Method for Uphill walks should be dveloped!

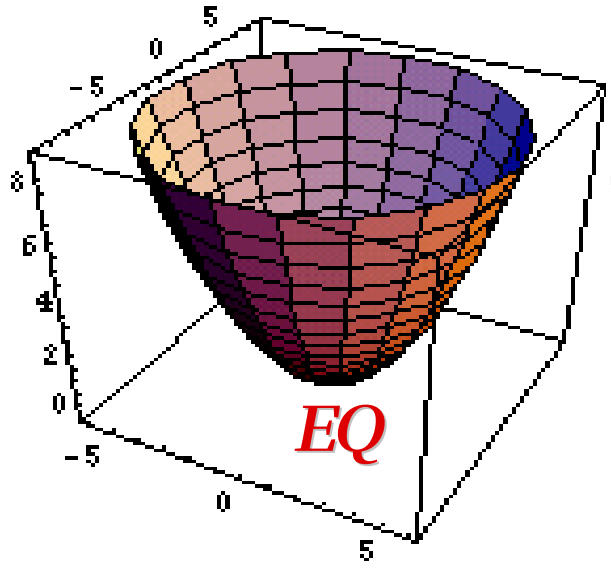
When Uphill walks become possible, Complete Reaction Route Mapping also become possible !

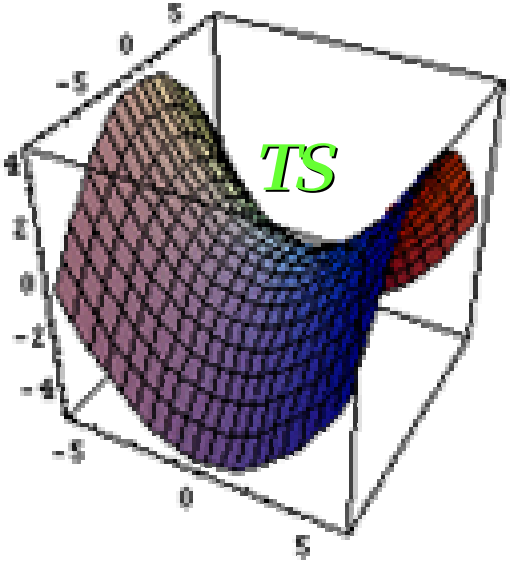


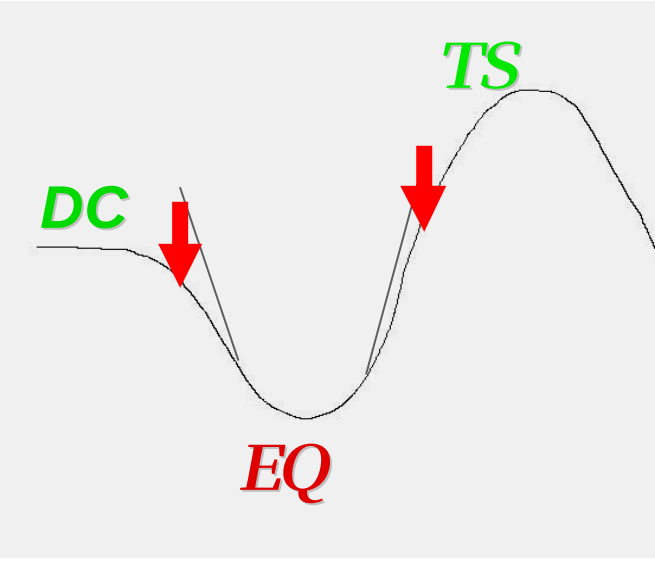
One after another algorithm!



How to find the entrance to a reaction route?





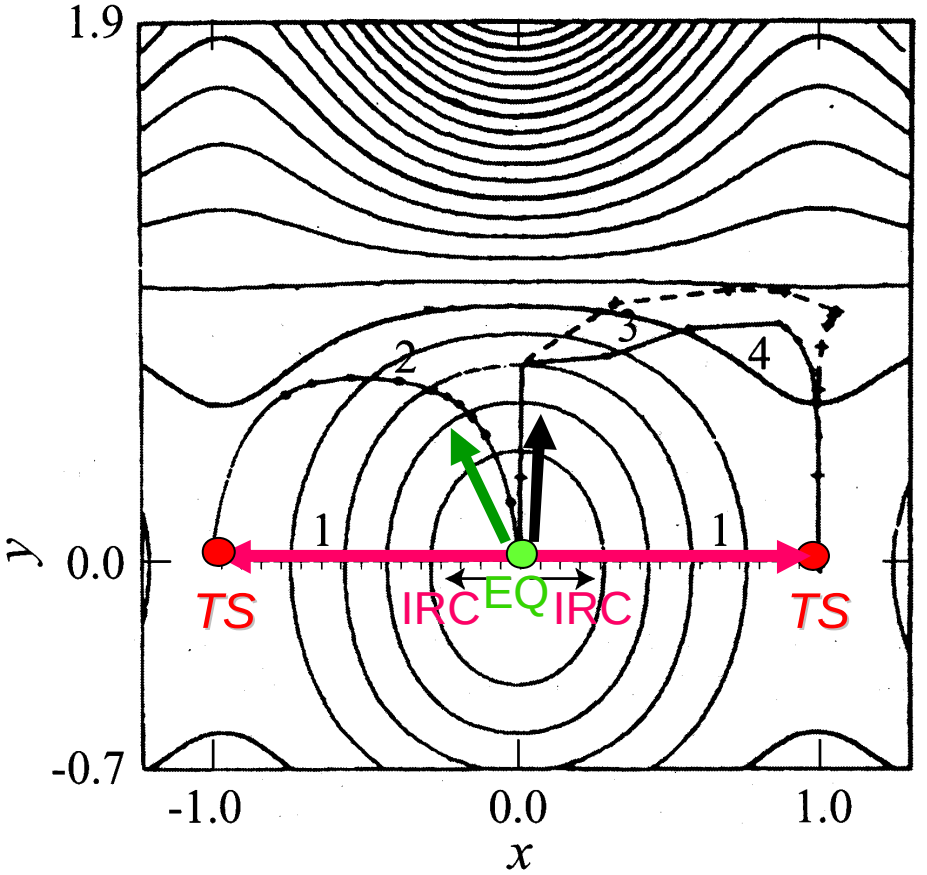


IDEA ： *Among all Directions surrounding an EQ Point,*

Search a Direction with the Maximum Downward Distortion!

Application to a model potential (1)

Cerjan - Miller Potential : *J.Chem.Phys.* 75, 2745 (1981).



1 This Work (SHS) ←

Scaled Hypersphere Search

2 SO Method: ←

Avashkin &Russo (1994)

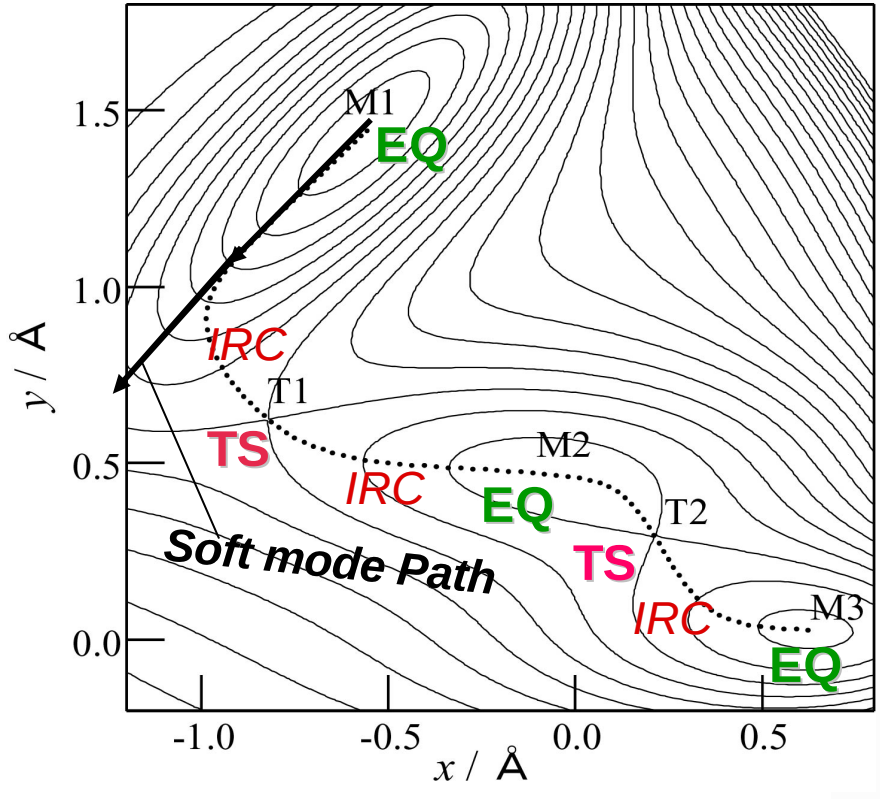
3, 4 EVF Method: ←

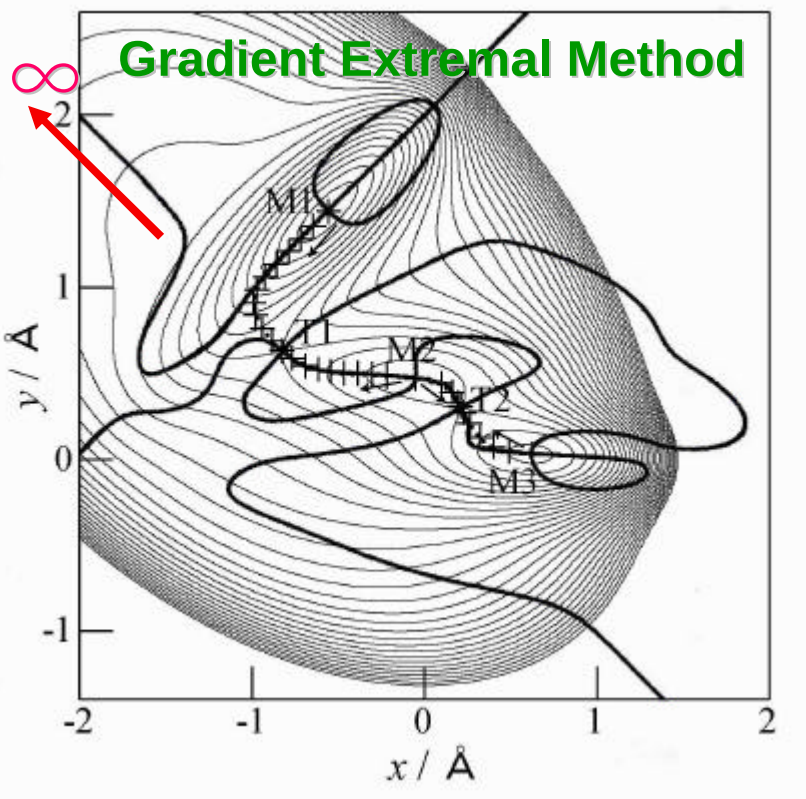
Banergee et al. (1983)

Earlier Methods tend to follow lower parts along soft modes.

Application to a model potential (2)

Müller - Brown Potential : *Theoret.Chim.Acta* 53, 75 (1979).





How to Find the Downward Distortion?

Scaled Hypersphere Search (SHS) Method

K. Ohno and S. Maeda, *Chem.Phys.Lett.* 384 (2004) 277

Scaled Normal Coordinate : $q_i = \lambda_i^{1/2} Q_i$

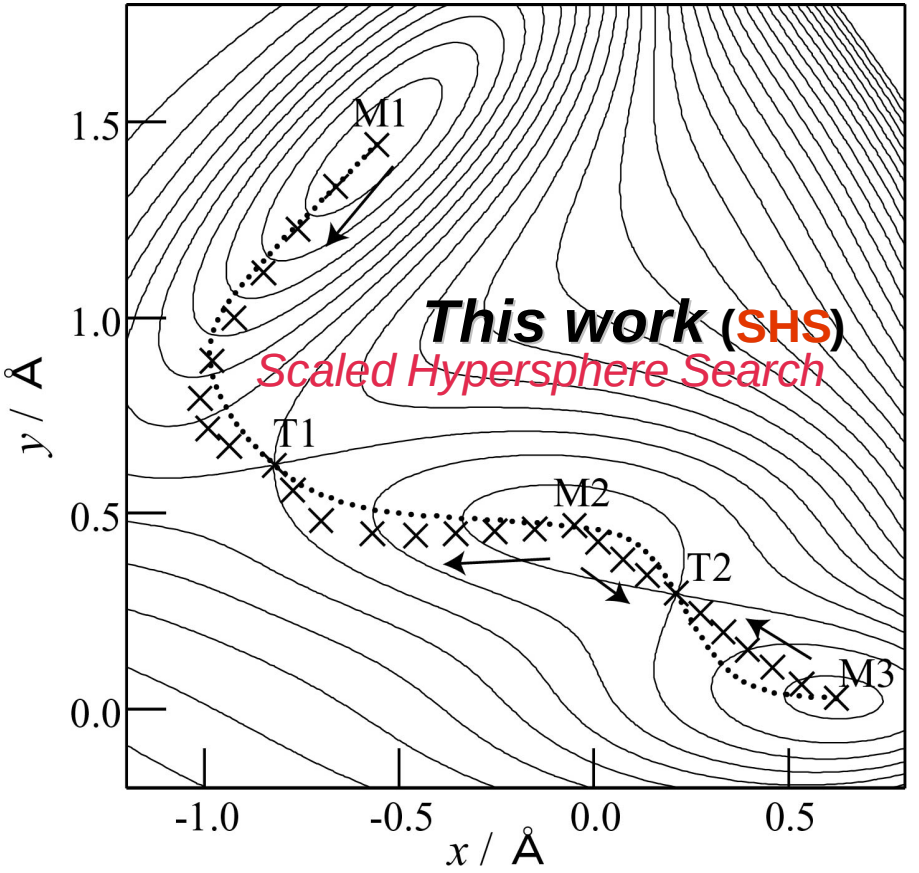
If the PES is harmonic, then the energy on the hypersphere becomes constant !

Thus, ***Downward Distortions*** on the real potential surface can easily be made by *a simple search of minima on the hypersphere !*

An efficient search becomes possible without try-and-errors. A complete search becomes possible because of the use of a closed surface..

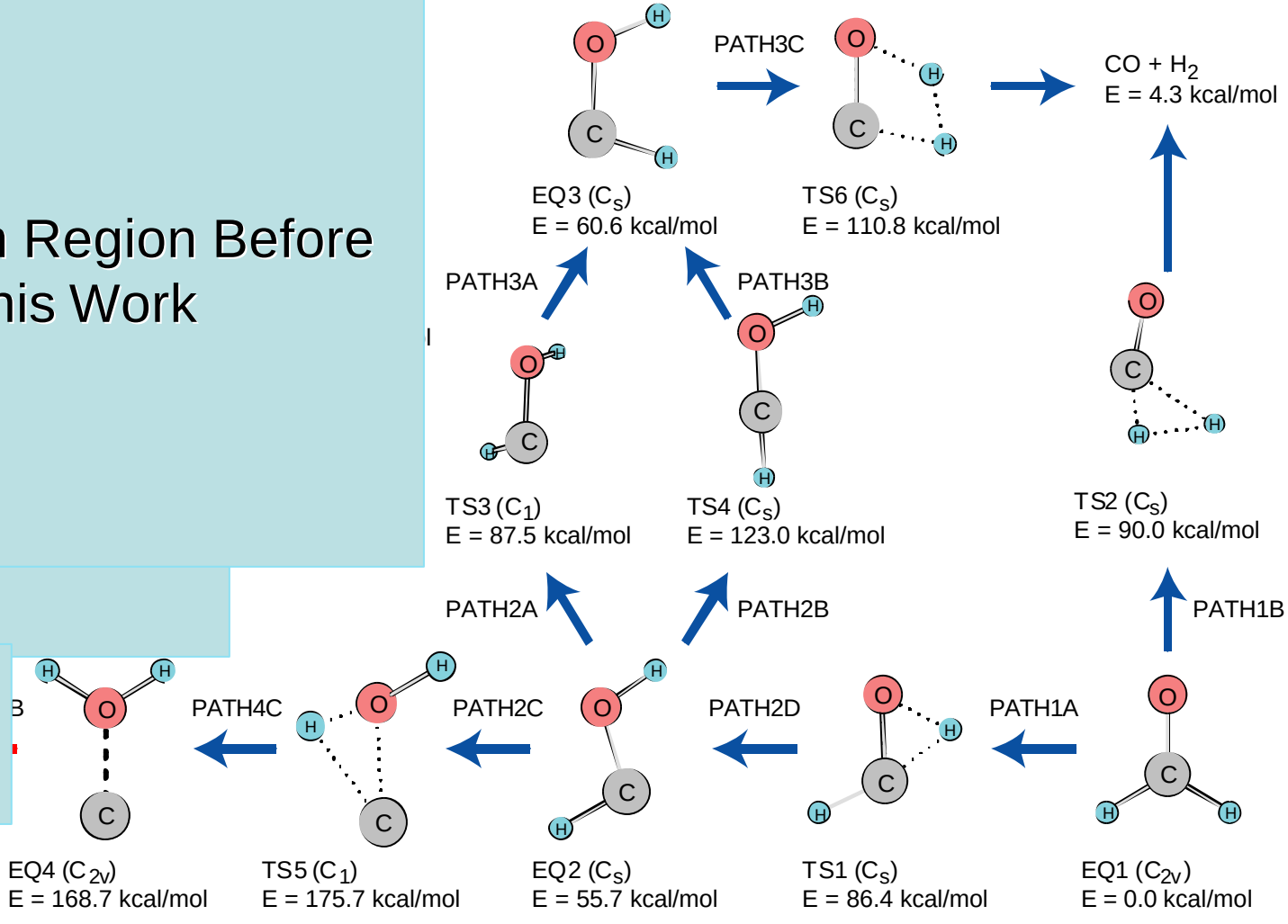
Application to a model potential (2)

Müller - Brown Potential : *Theoret.Chim.Acta* 53, 75 (1979).



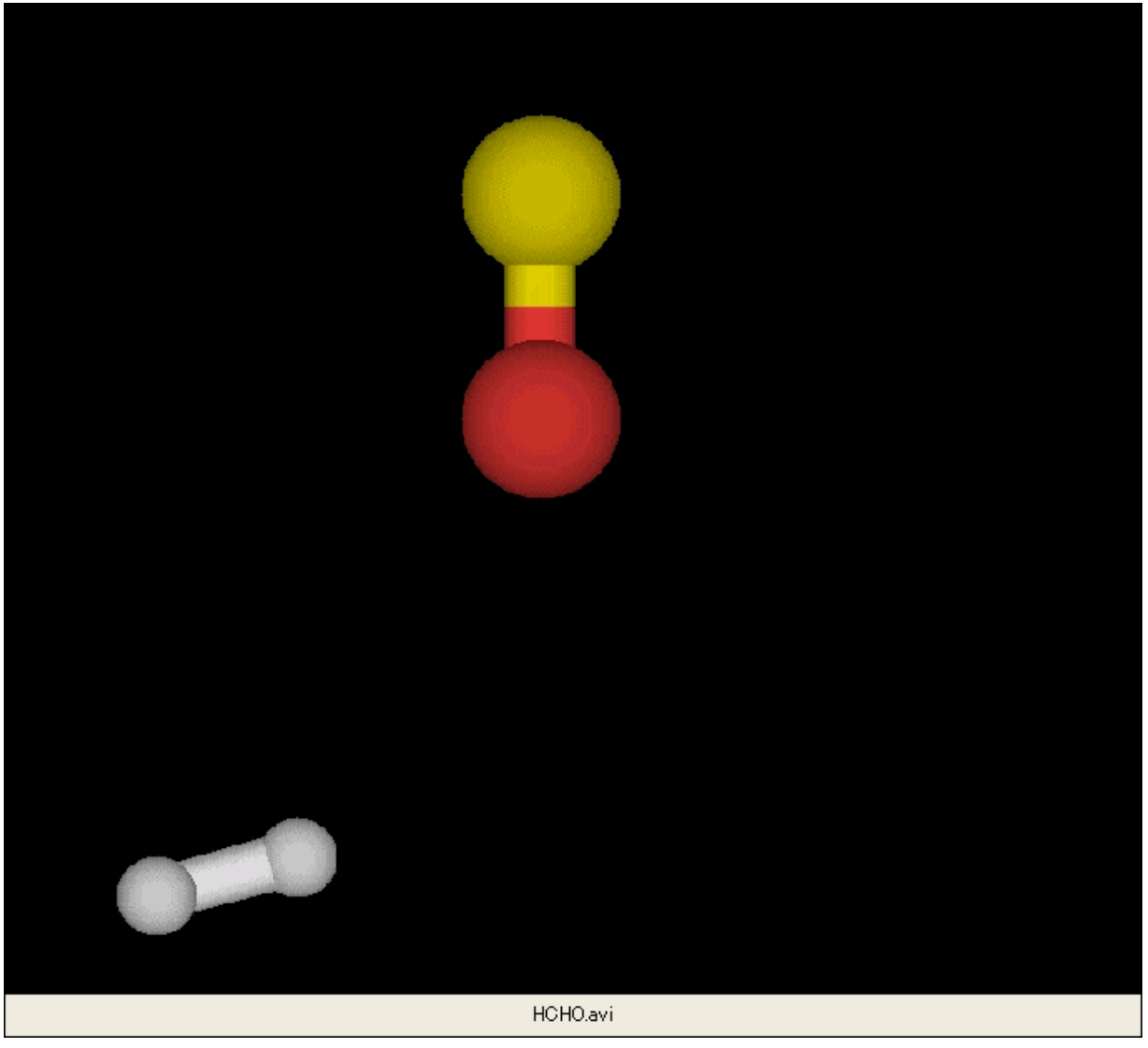
Global Search for HCHO System

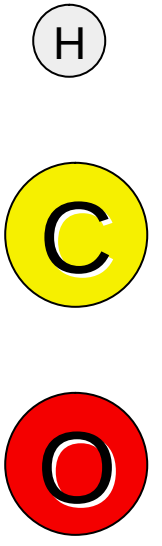
Unknown Region Before This Work



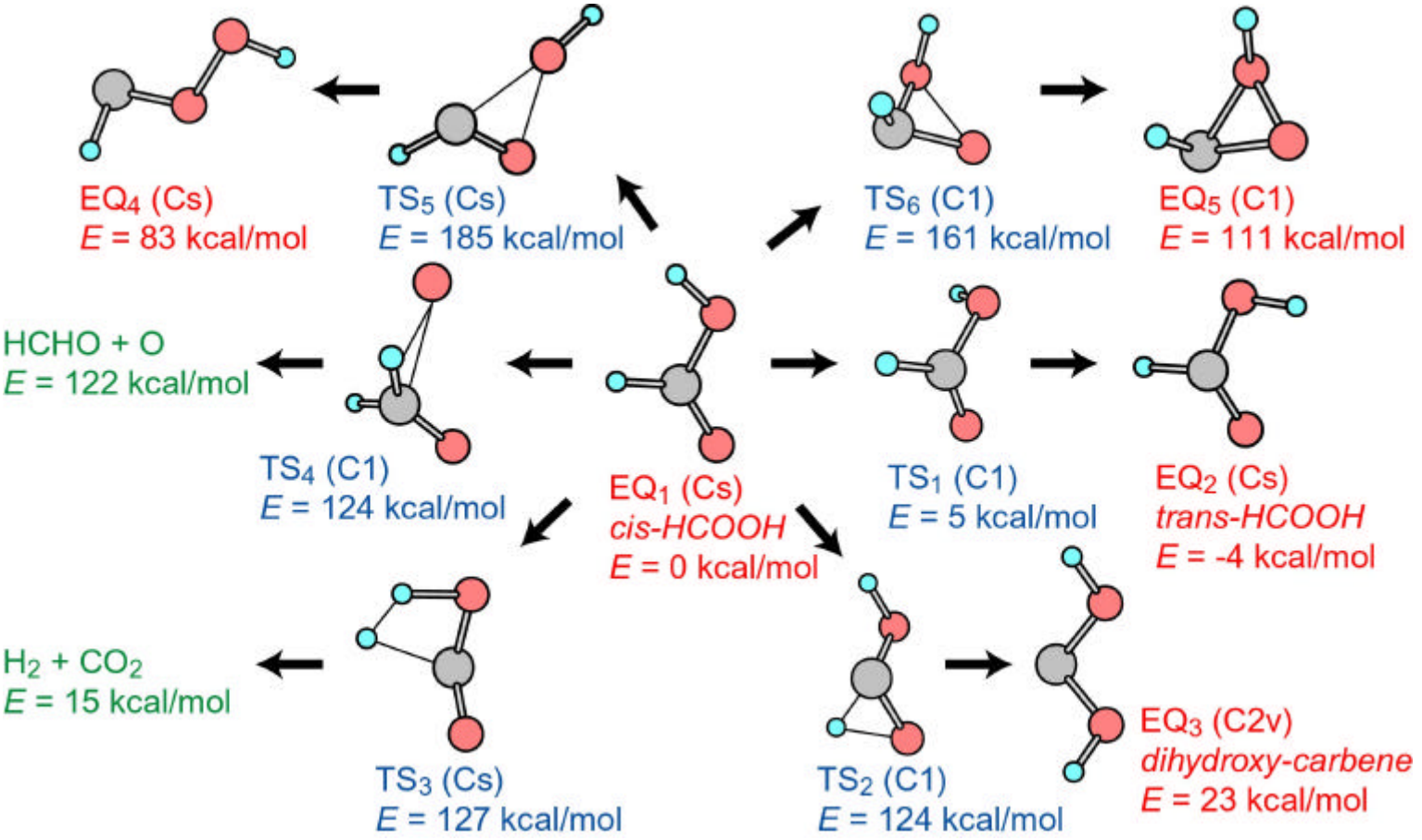
New Reactions **Known Reactions**

$$H_2 + CO \longleftrightarrow HCHO$$

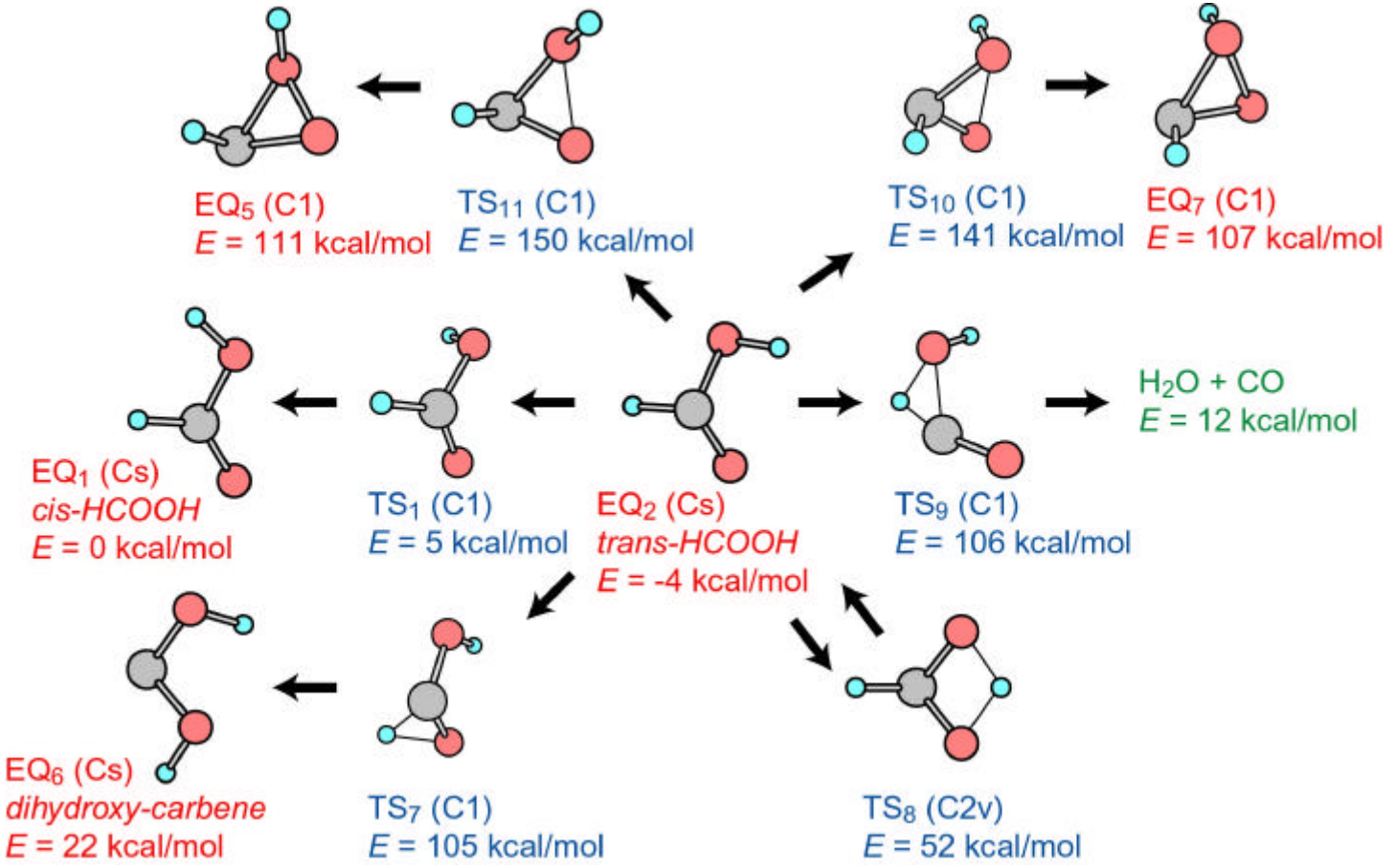




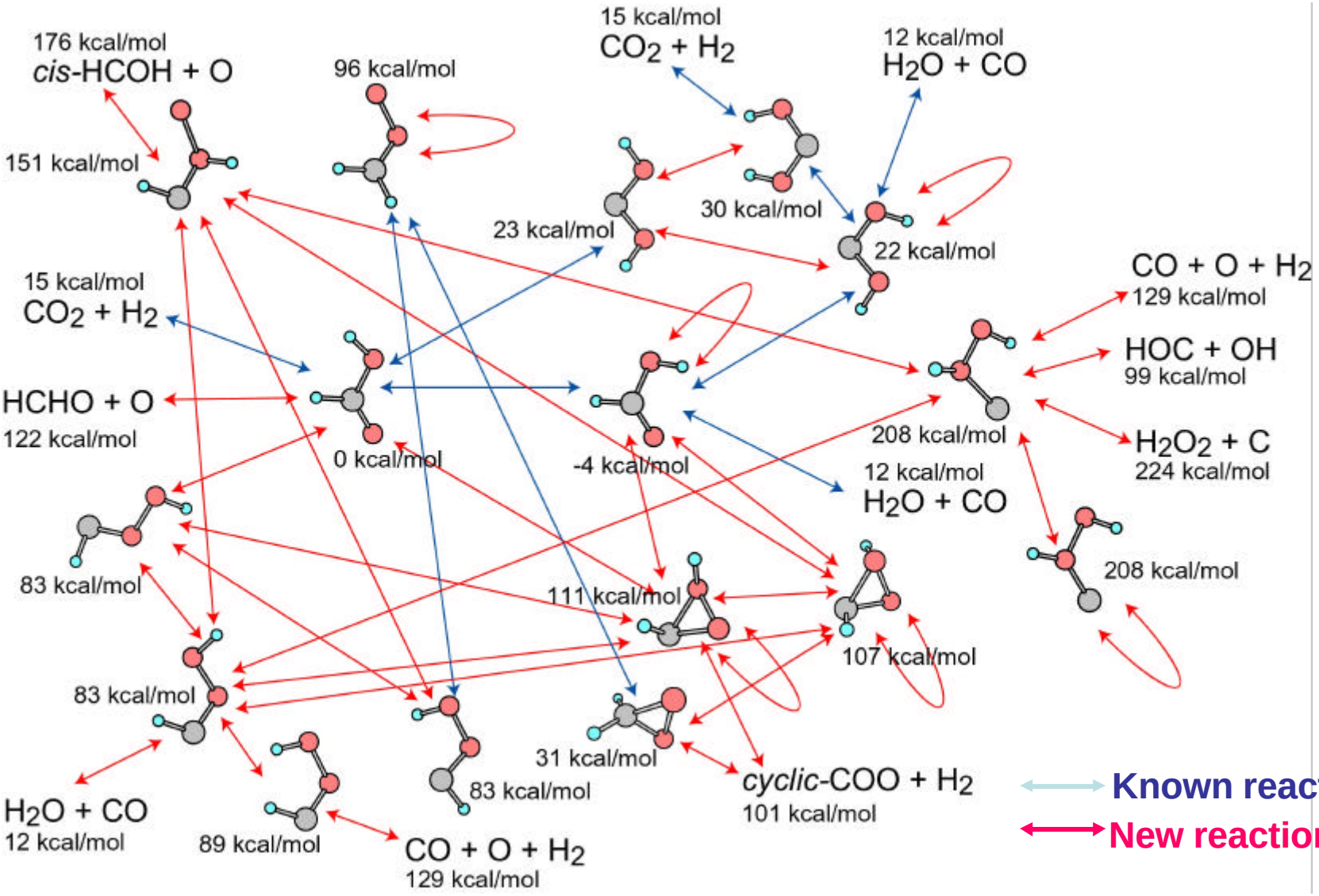
Map around *cis*-HCOOH



Map around *trans*-HCOOH



Global Search for HCOOH System

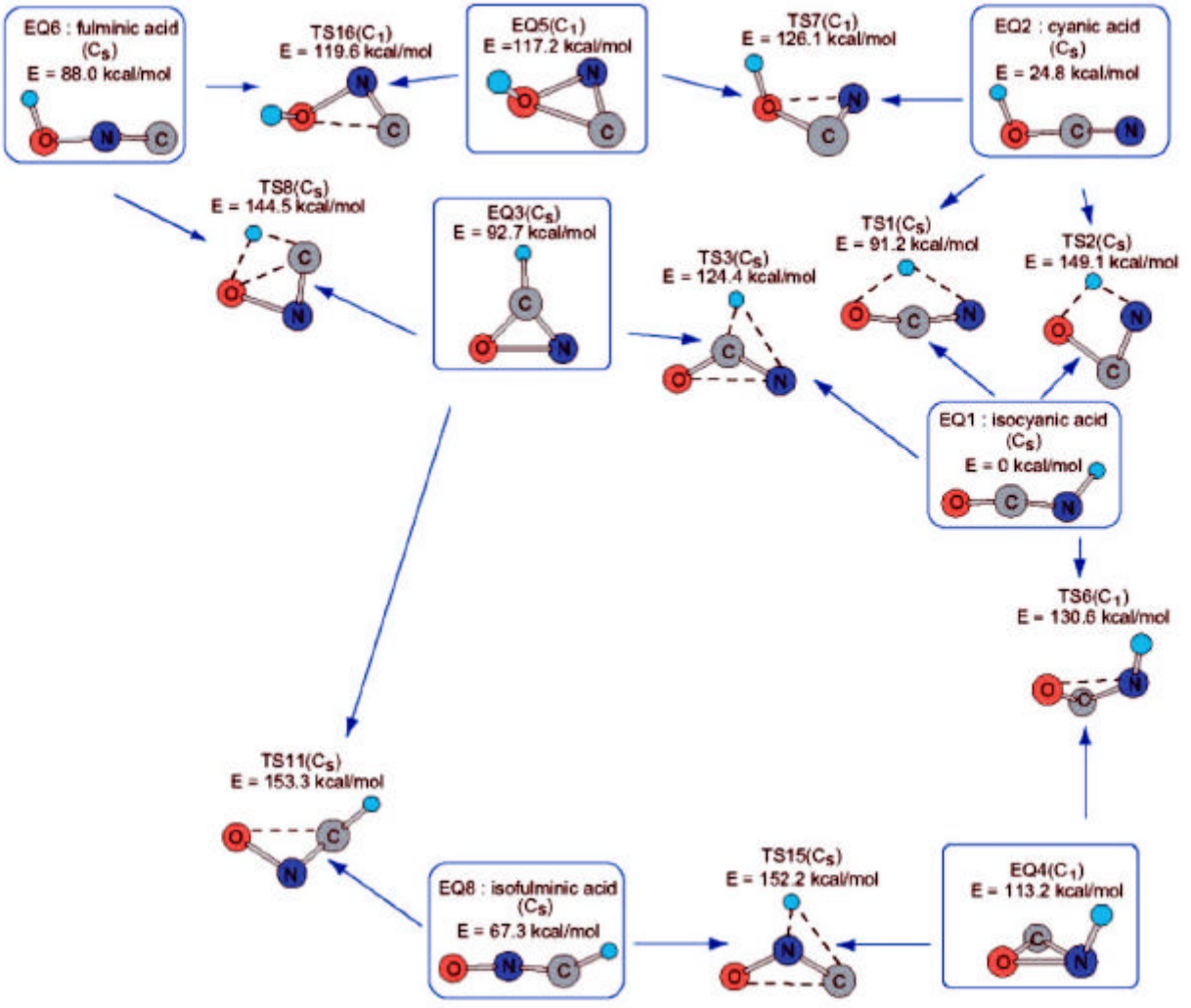


16 EQ and 46 TS were found 8 EQ and 36 TS were newly found

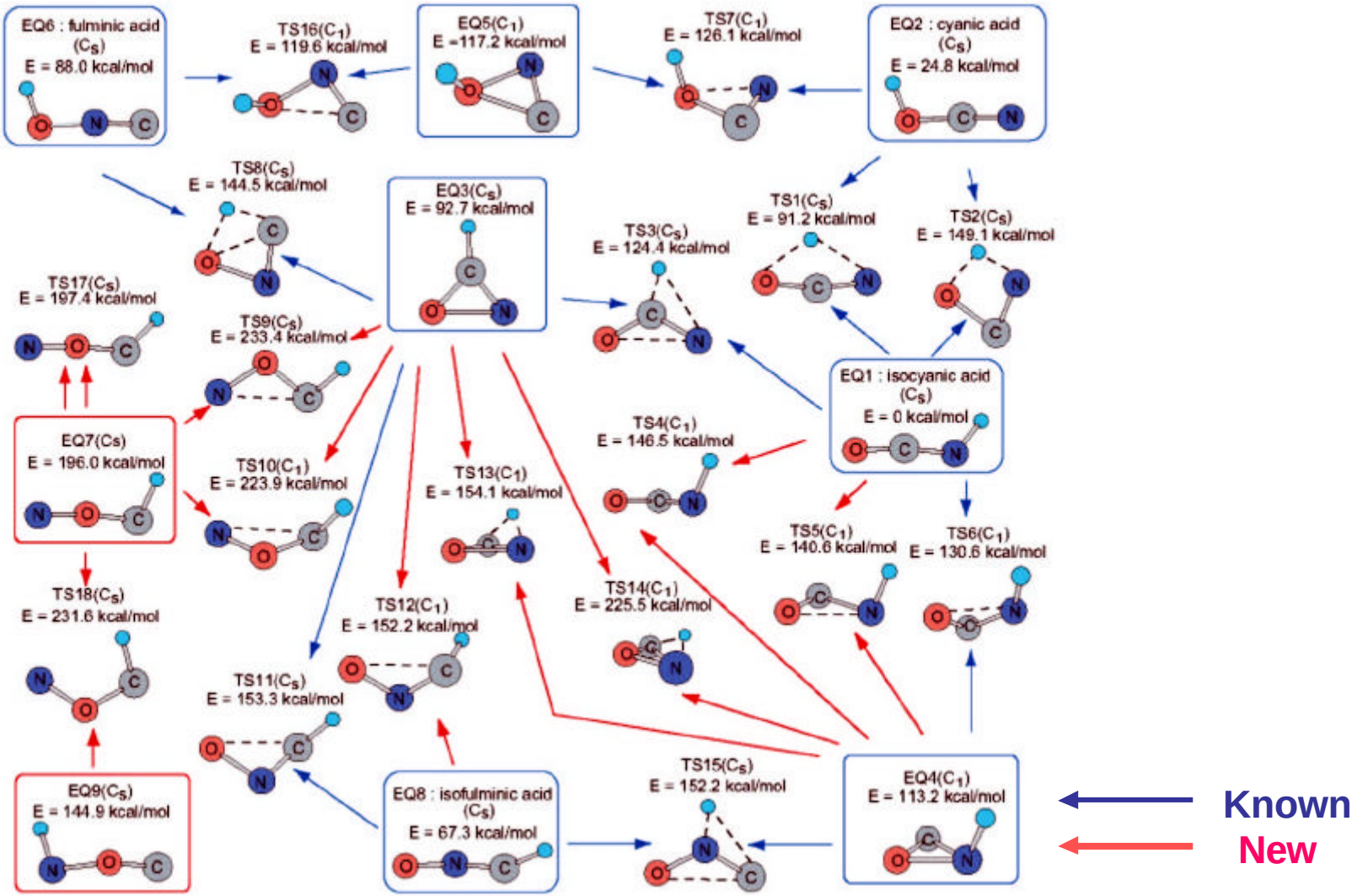
Isomerization Routes of HOCN

(Before This Work)

7EQ and 9 TS



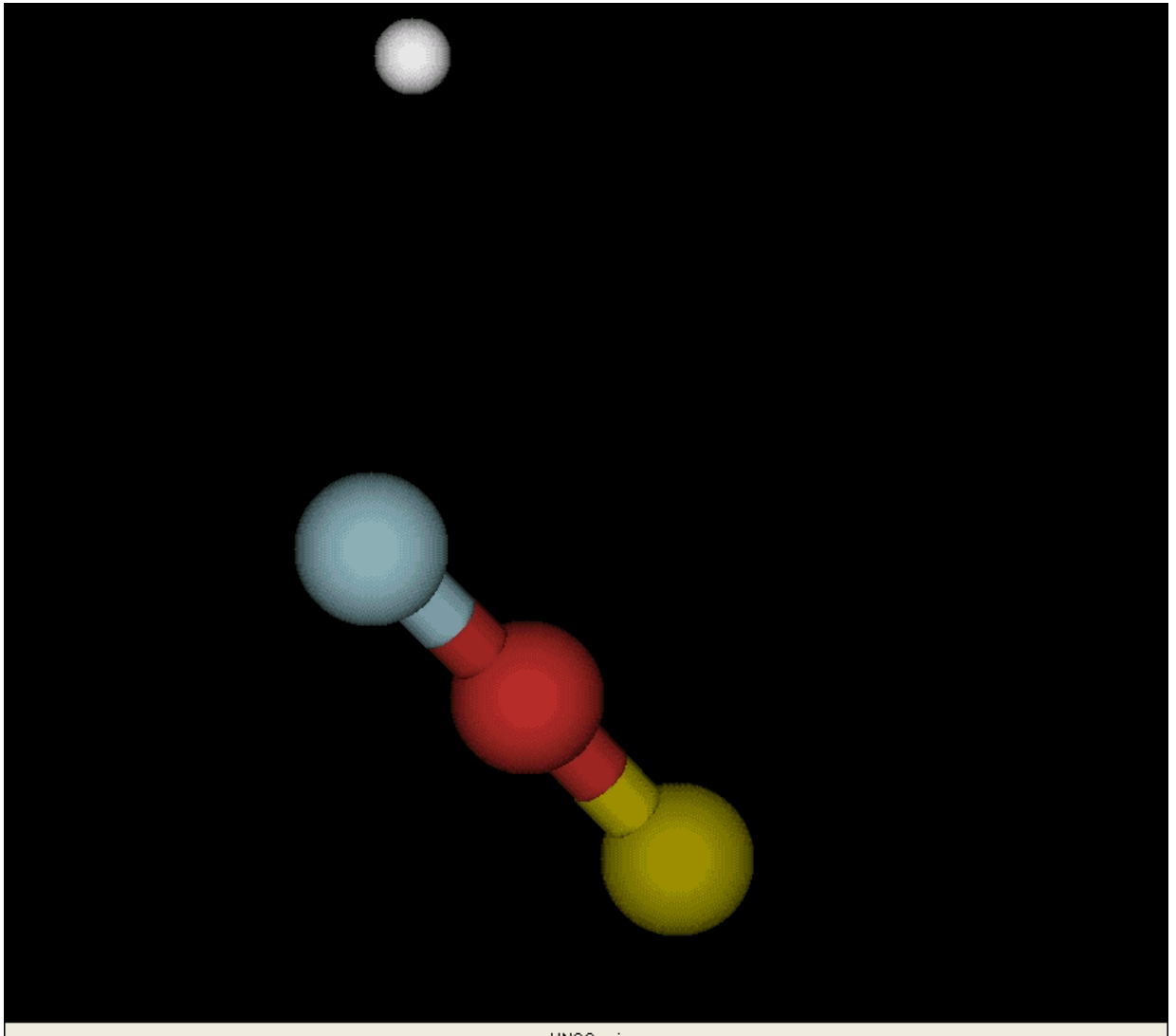
Global Search for Isomerization of HOCN



9 EQ and 18 TS were found

2 EQ and 9 TS were newly found

Reactions of H+NOC



H

N

O

C

Application of the SHS Method to finding a new synthetic route with no byproducts recommended by economy and environments

IDEA

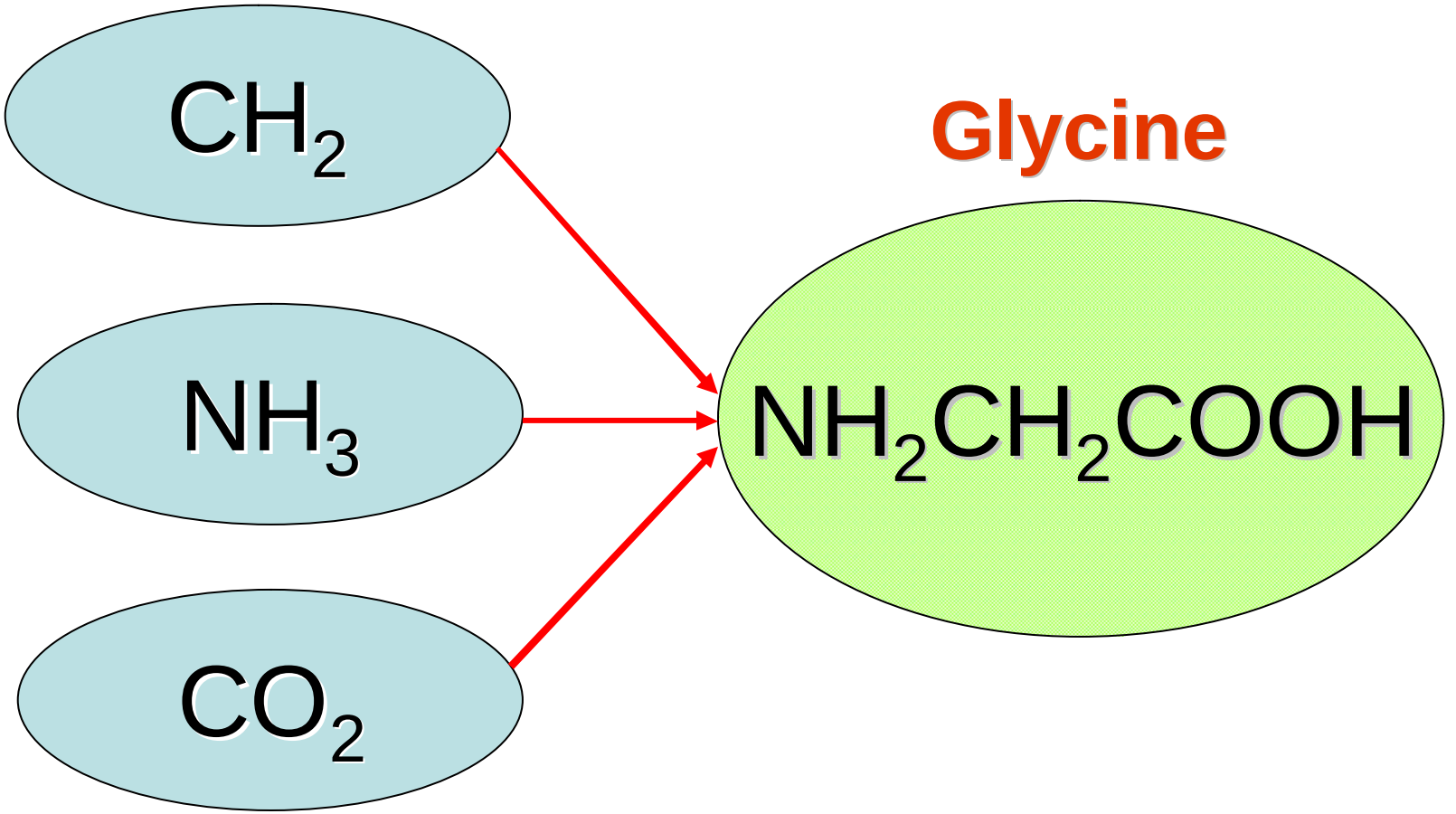
- Find Dissociation Channels by SHS starting from the aimed compound (*A*)

$$A \rightarrow B+C$$

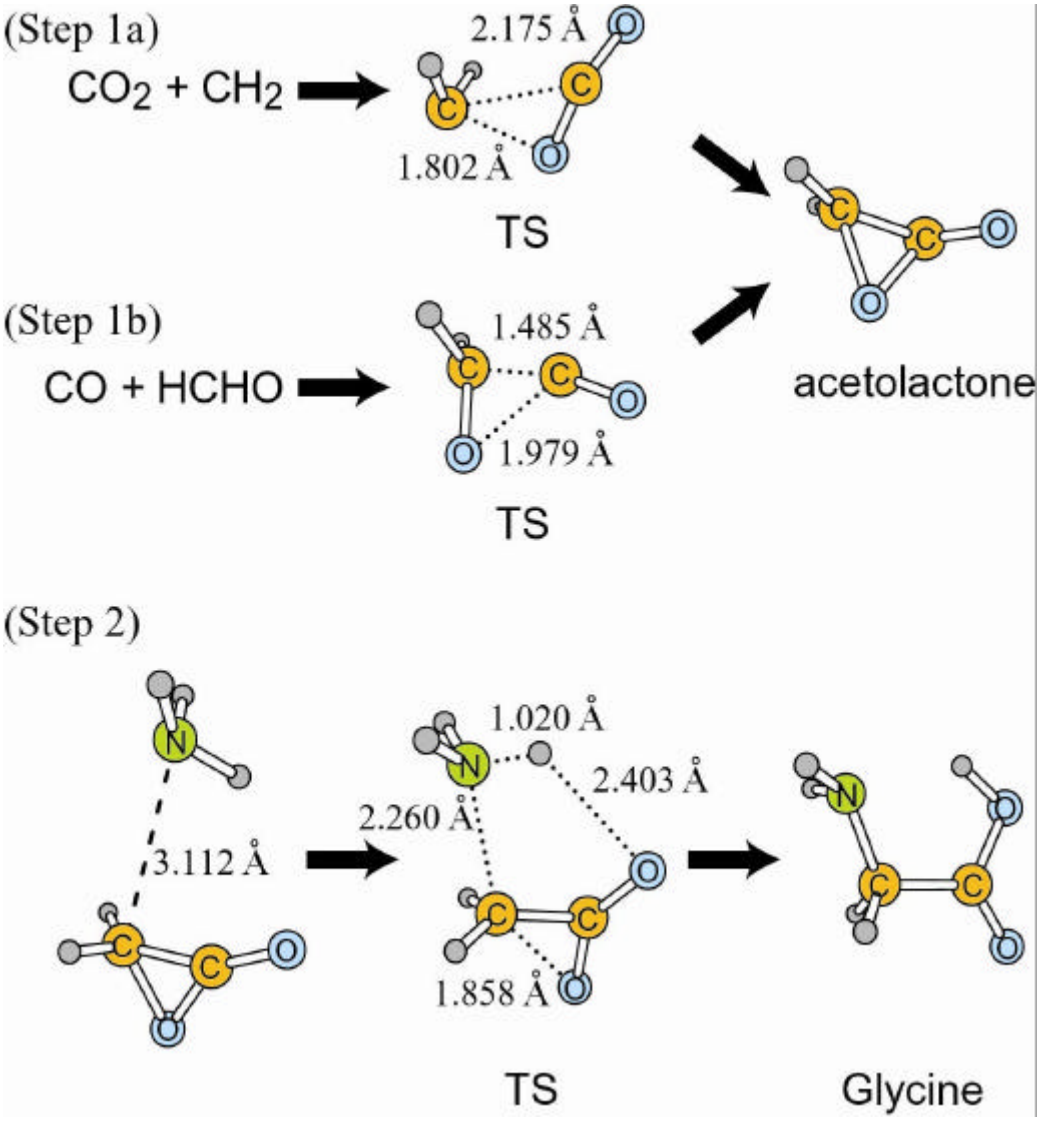
- Trace back to the initial compounds from the dissociation products (*B* and *C*)

$$B+C \rightarrow A$$

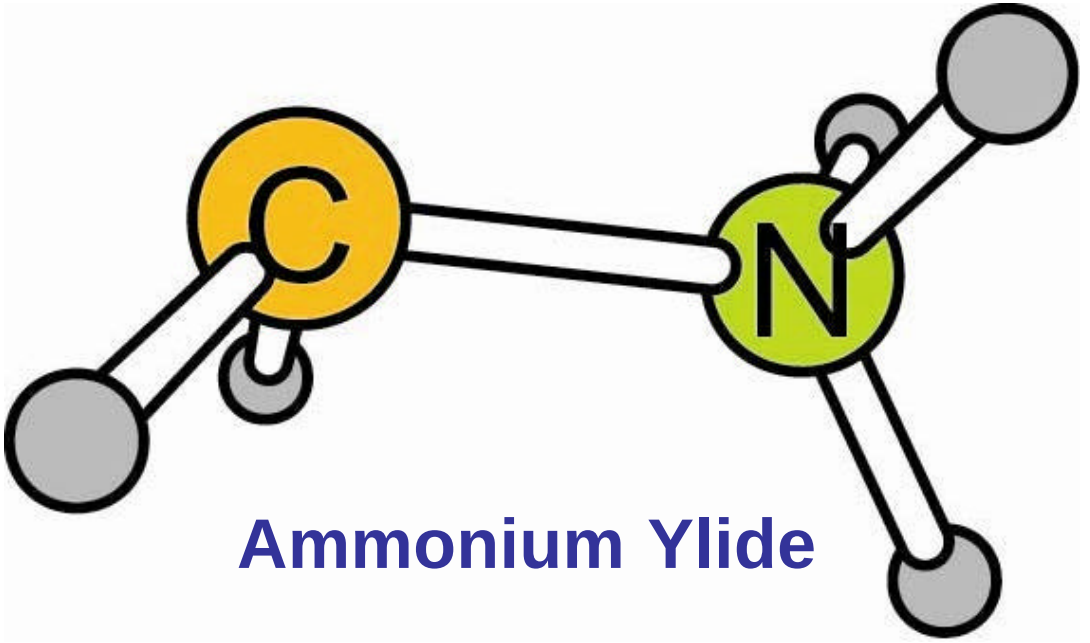
New synthetic routes of Amino acids from simple molecules



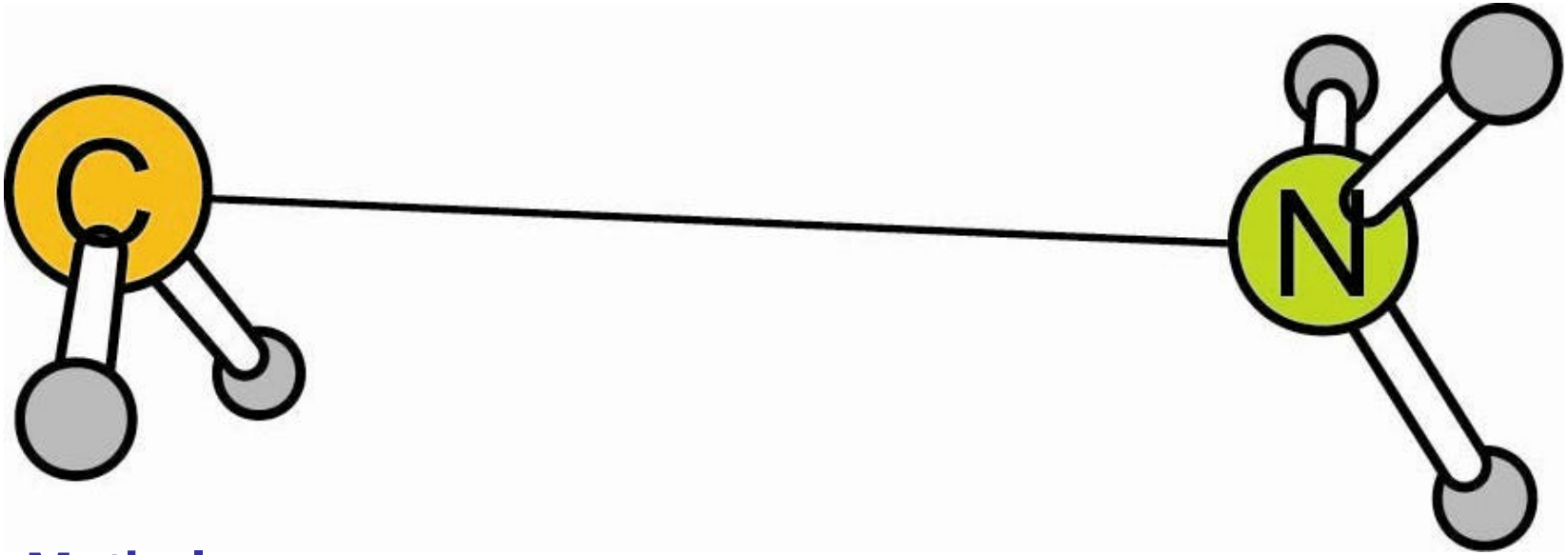
Glycine Synthesis via α-lactone



Glycine Synthesis via Ylide from CH_2 and NH_3

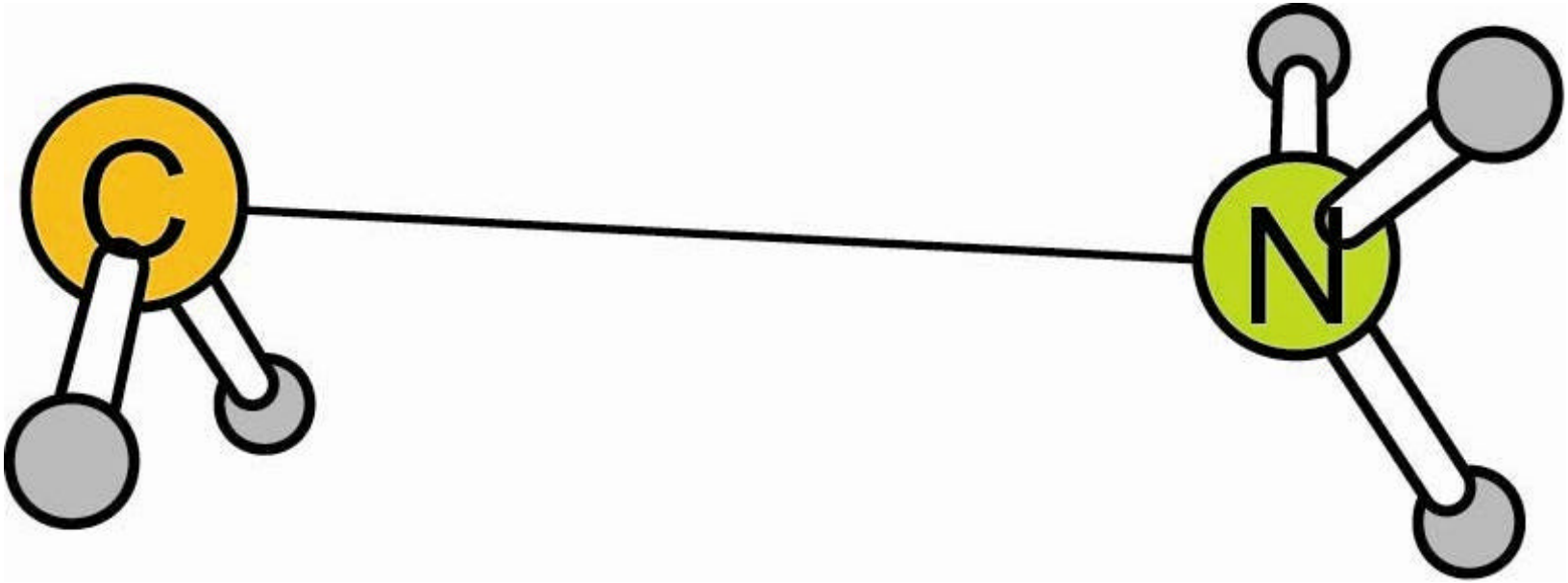


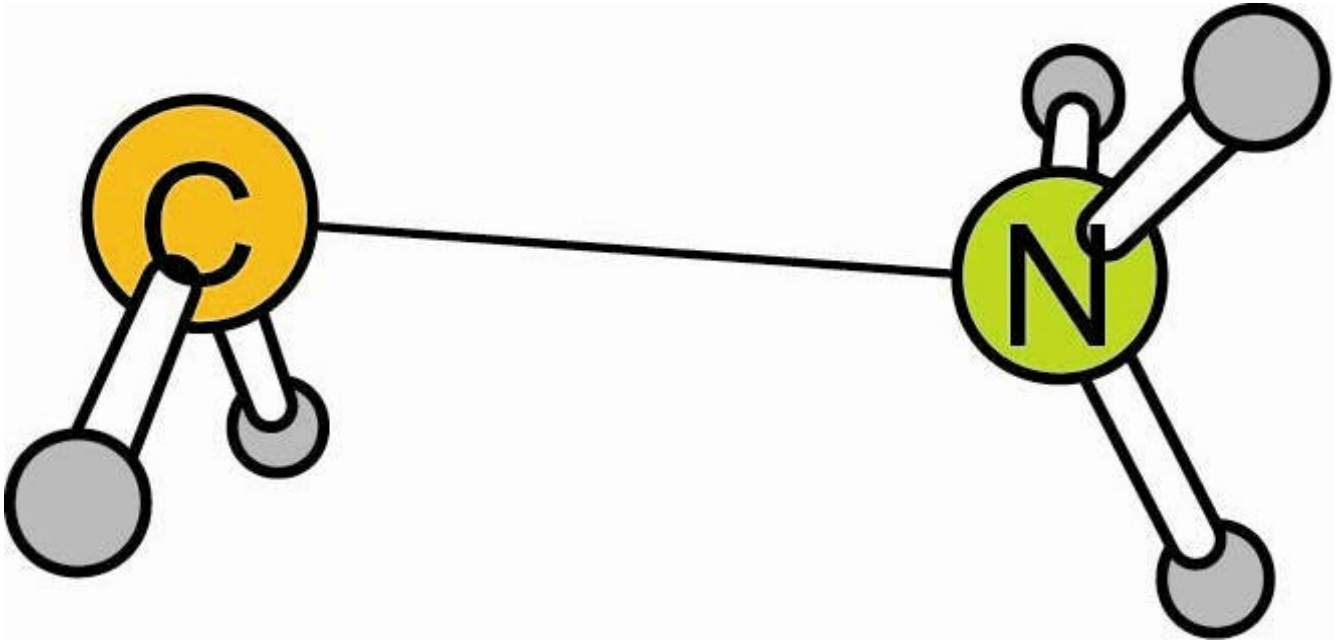
Ammonium Ylide

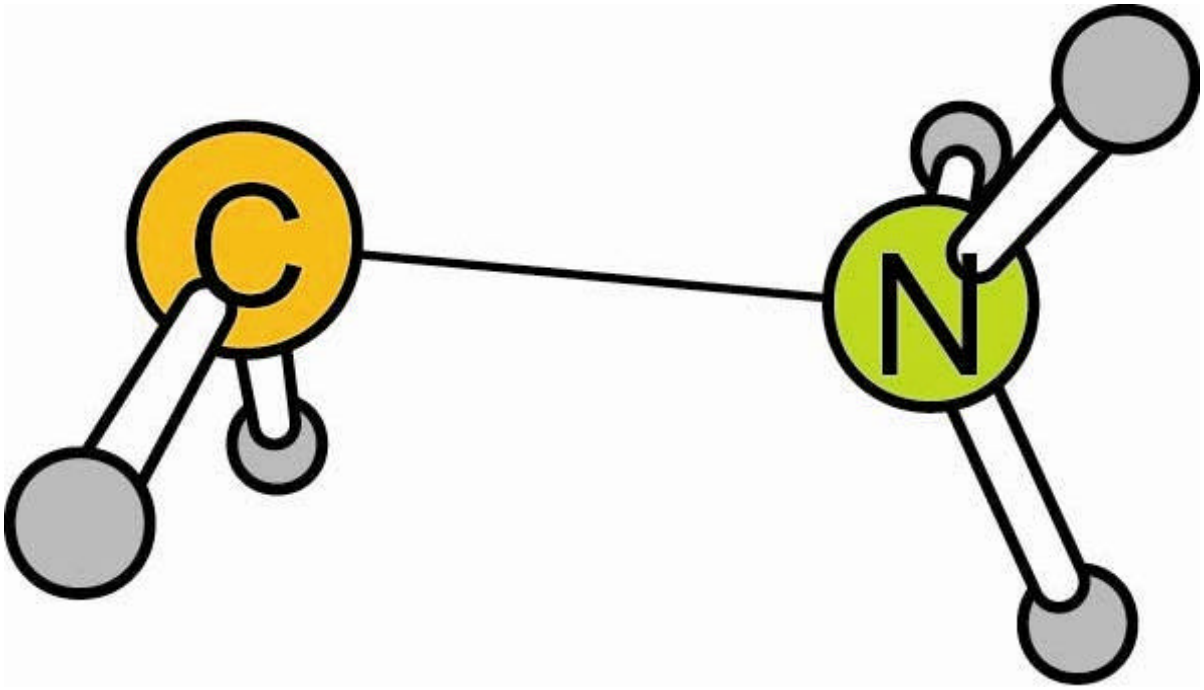


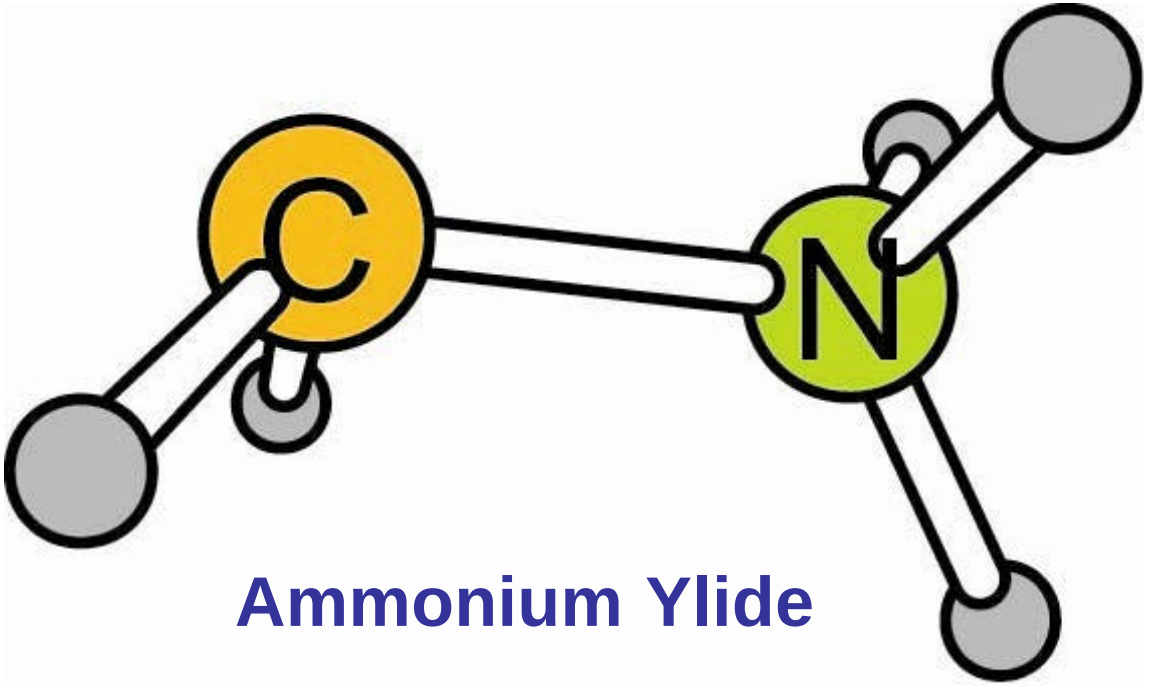
Methylene

Ammonia


C
N

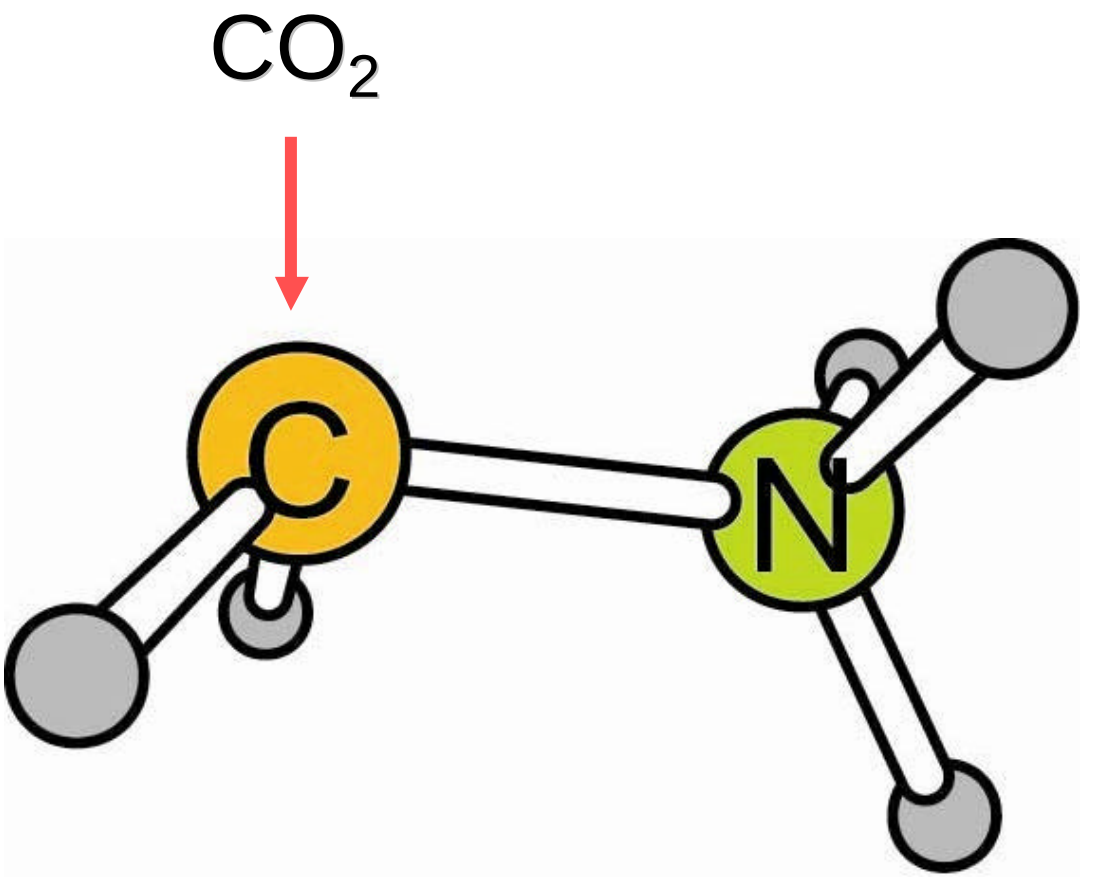

C
N


C
N

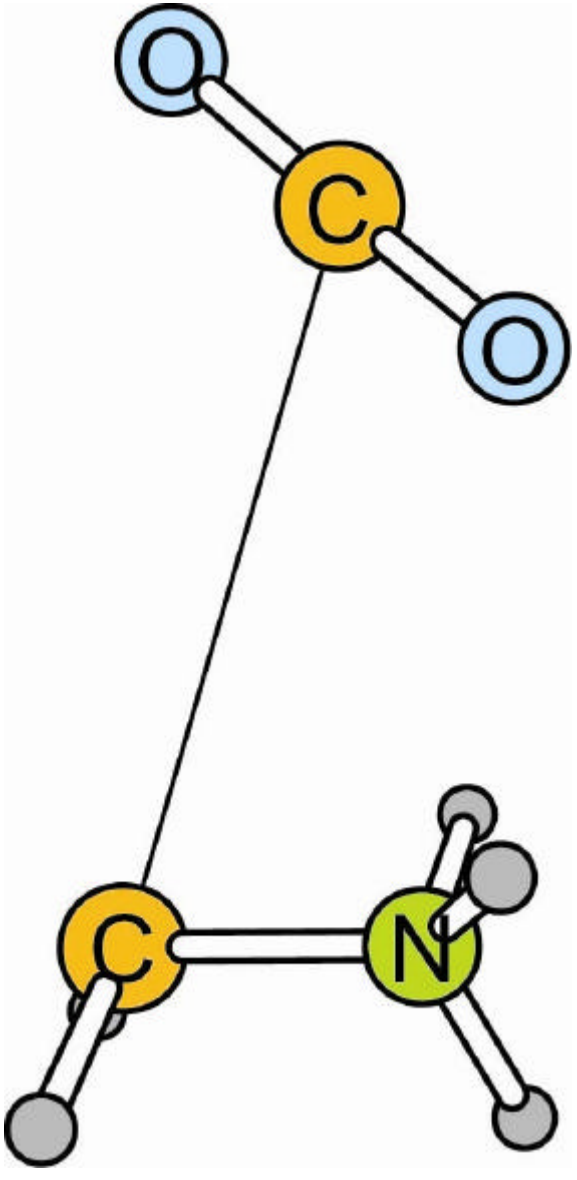


Ammonium Ylide

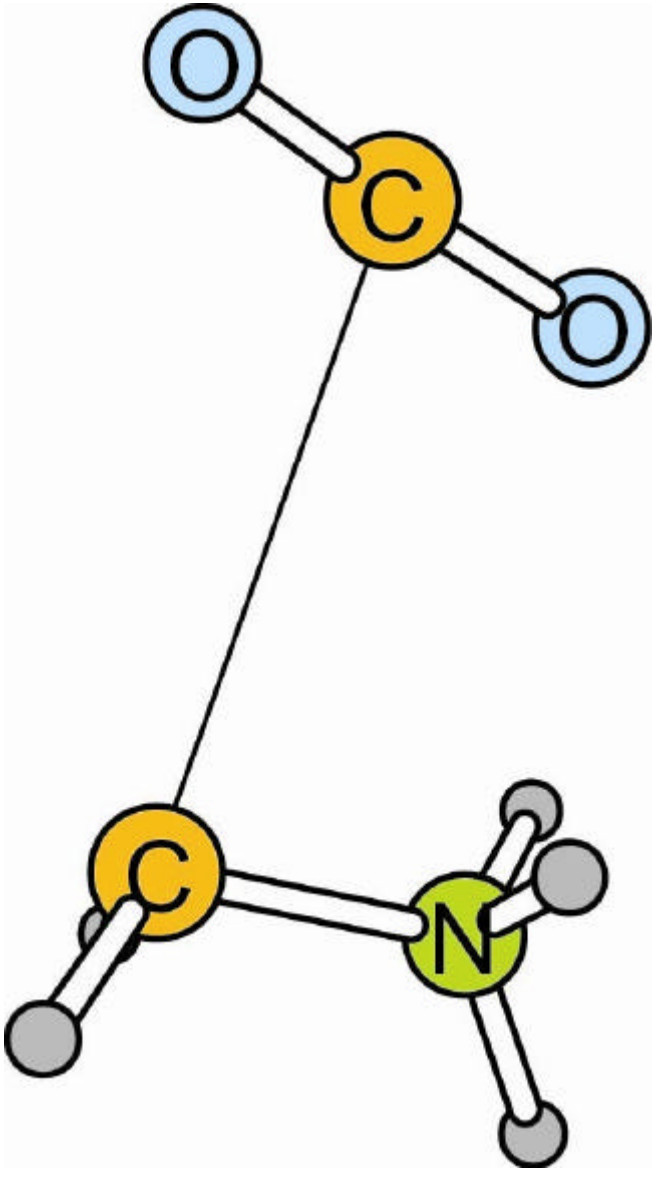
Glycine Synthesis via Carboxylation of Ammonium Ylide

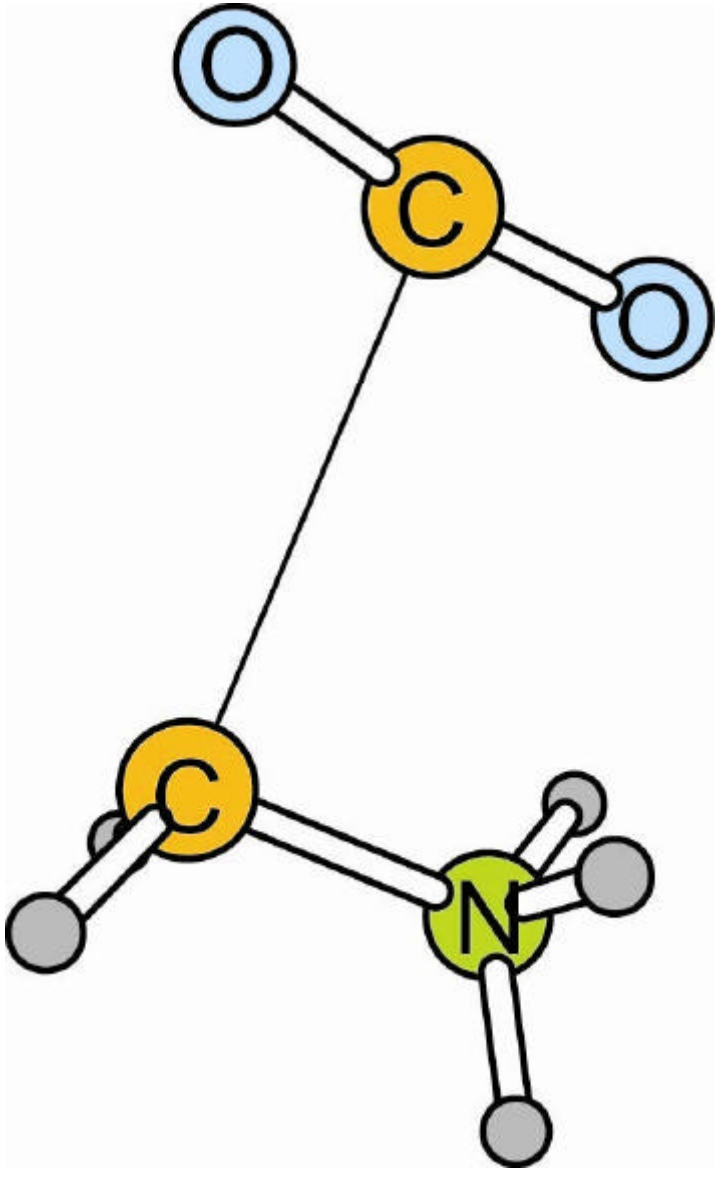


Carbon Dioxide



Ammonium Ylide


O
C
O
C
N


O
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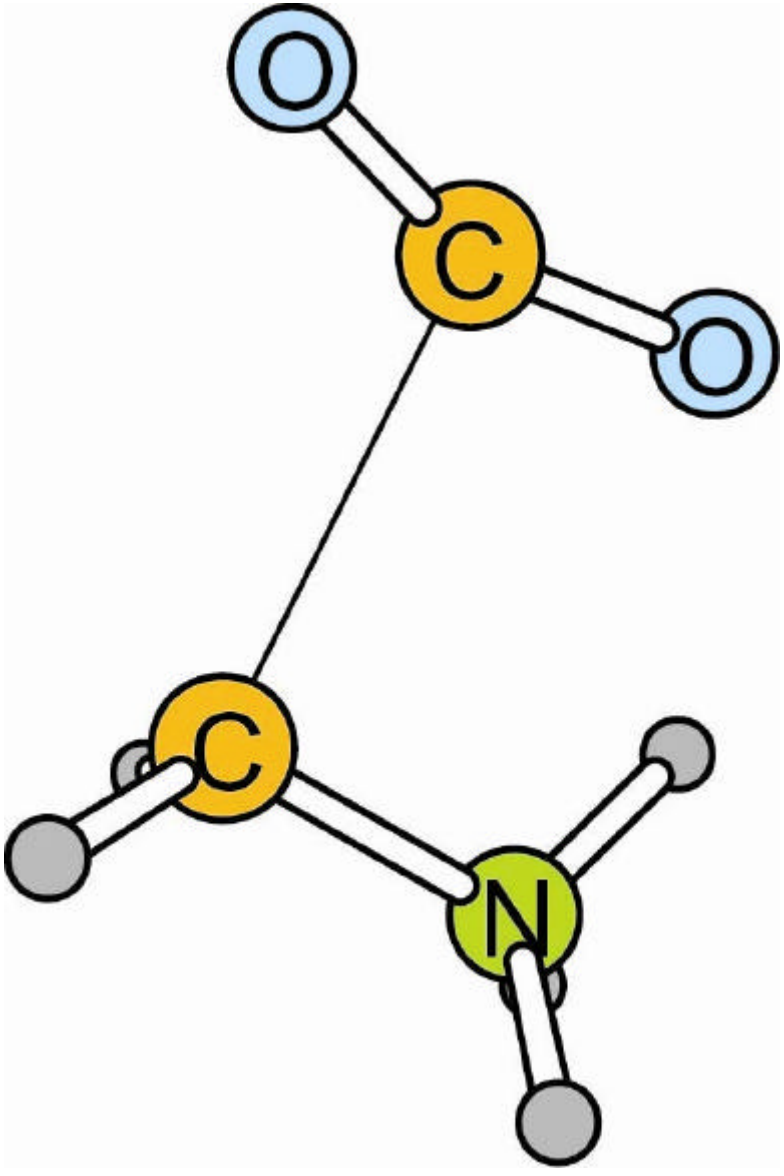
O
C
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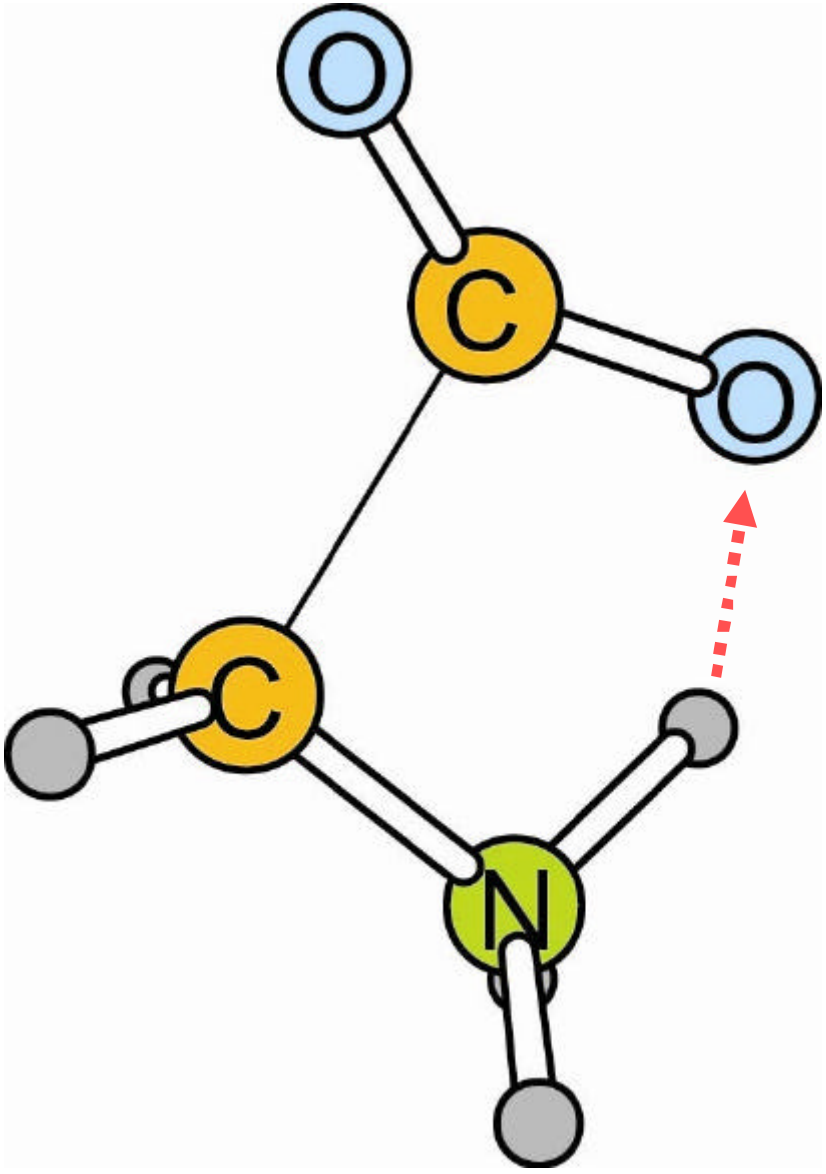
O
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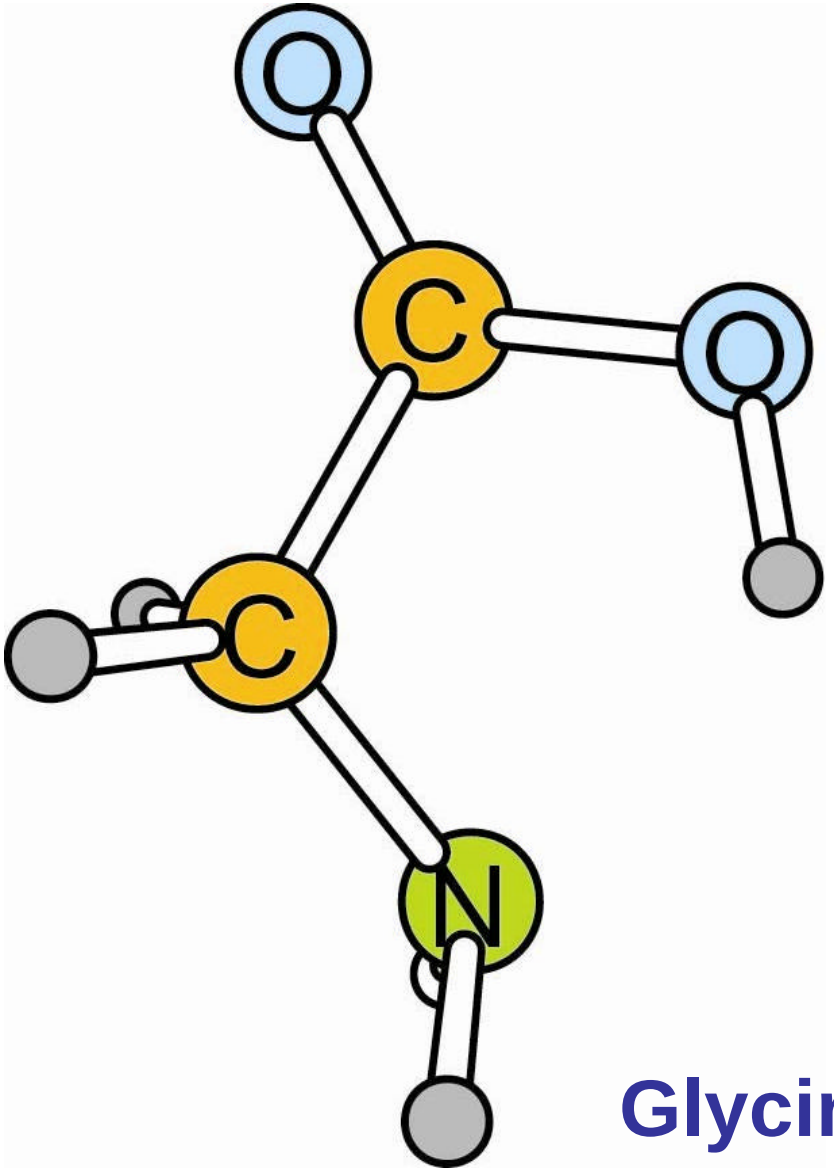


Glycine

$$CH_2 + NH_3 + CO_2 \rightarrow H_2NCH_2COOH$$

Summary

Using Scaled Normal Coordinates,

Scaled Hypersphere Search (SHS) Algorithm

is developed for finding All Reaction Pathways on the Potential Energy Surface.

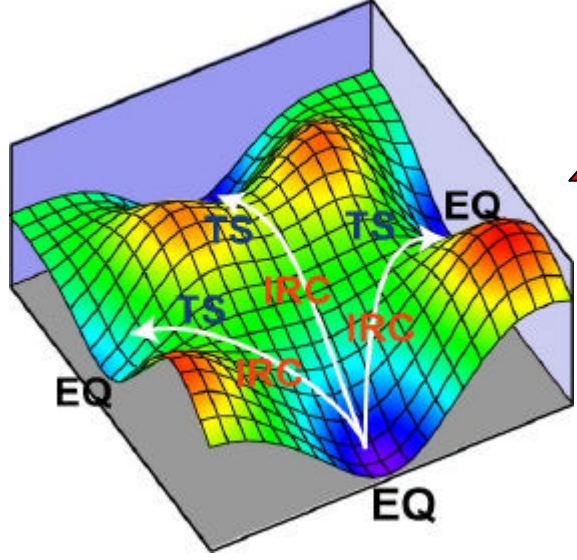
For a Given Chemical Composition

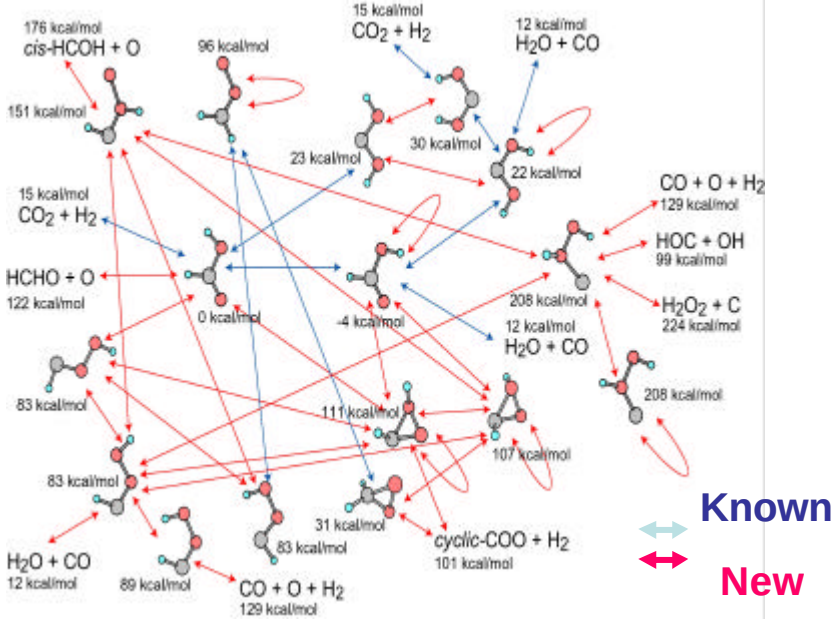
1) All Isomers
2) All Dissociation Paths
3) All Synthetic Paths

All Reaction Pathways can be Discovered.

This technique may be used to construct an *Automated Reaction Simulator*

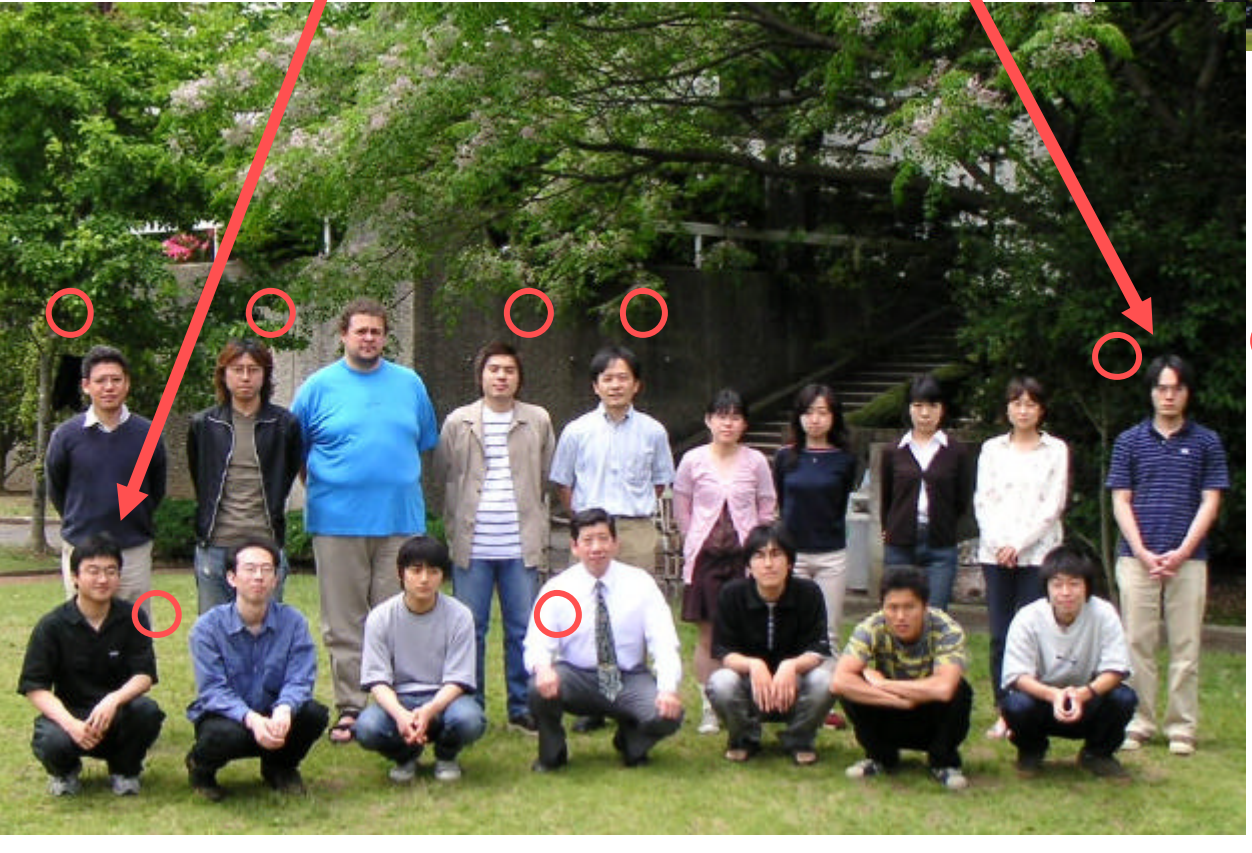
based on complete mapping of potential energy surface.



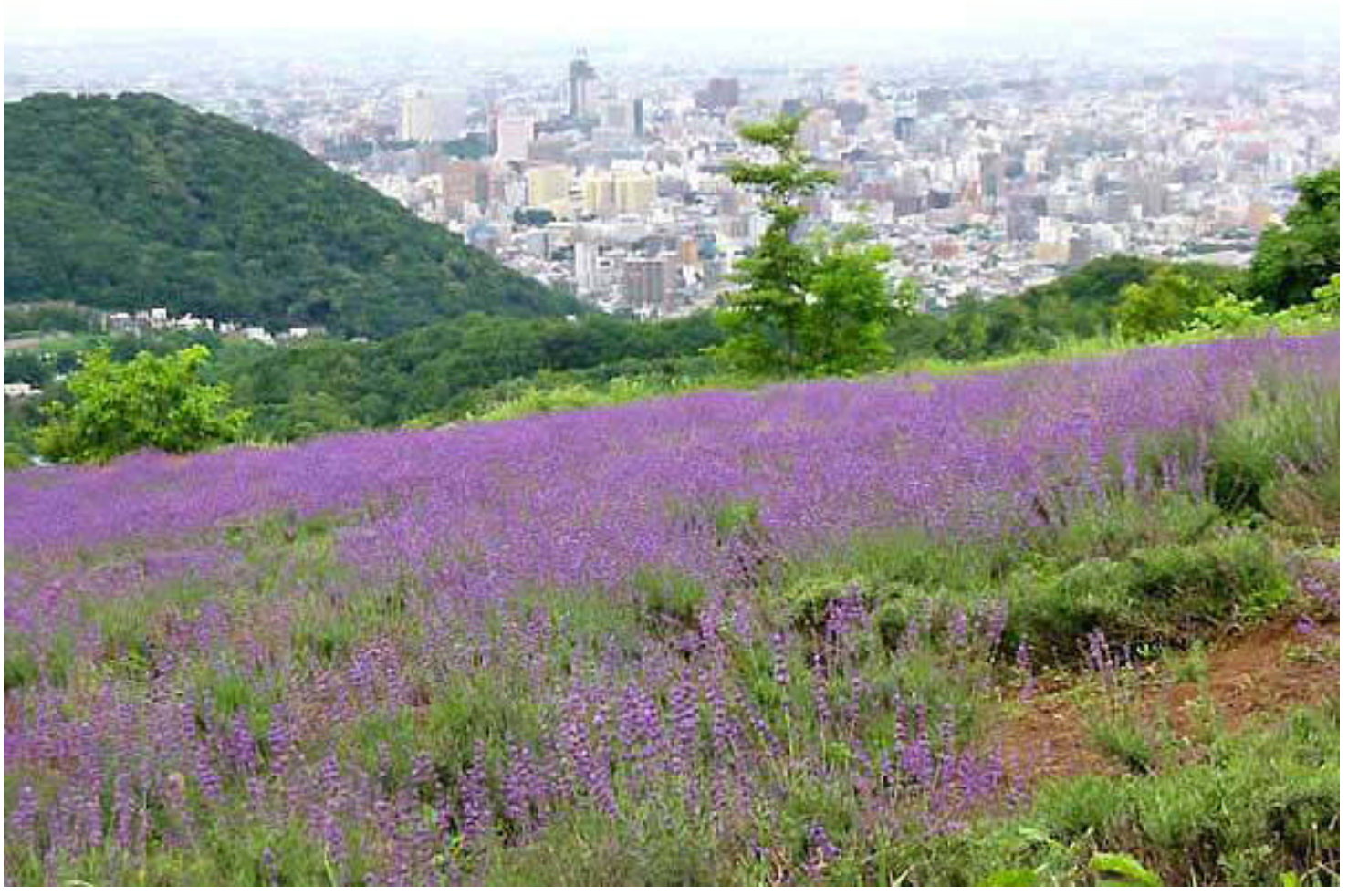


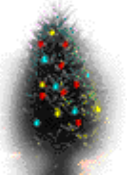
○ ***Participants of this Conference***
&
→ ***Collaborators of this work***

Satoshi Maeda (JSPS Fellow:DC1)
Tsuyoshi Hirose (B4)



A View from a Saddle Point





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Development of a New Algorithm for Finding All Reaction Pathways

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