40th “A. CORBELLA” INTERNATIONAL SUMMER SCHOOL ON ORGANIC SYNTHESIS – ISOS 2015

problem section
Problem 1 - Organocatalysis: mechanism

a) Is the compound A chiral?

b) For the reaction, please provide a reasonable mechanism.

A + \text{PhCl, 25 °C, 42 h}
\quad \text{Yield = 51%, ee = 84%}

\text{Boc}
\begin{align*}
\text{N} & \quad \text{O} \\
\text{Boc} & \quad \text{O} \\
\text{N} & \quad \text{O} \\
\text{N} & \quad \text{H}
\end{align*}

\begin{align*}
\text{N} & \quad \text{S} \\
\text{N} & \quad \text{N} \\
\text{CF}_3 & \quad \text{CF}_3
\end{align*}

\text{NH}_2 + \text{NH}_2

10 \text{ mol%}

\begin{align*}
\text{N} & \quad \text{O} \\
\text{N} & \quad \text{H}
\end{align*}

\text{Boc}

\begin{align*}
\text{N} & \quad \text{S} \\
\text{N} & \quad \text{N} \\
\text{CF}_3 & \quad \text{CF}_3
\end{align*}

\text{NH}_2 + \text{NH}_2

10 \text{ mol%}

\begin{align*}
\text{N} & \quad \text{O} \\
\text{N} & \quad \text{H}
\end{align*}

\text{Boc}

\begin{align*}
\text{N} & \quad \text{S} \\
\text{N} & \quad \text{N} \\
\text{CF}_3 & \quad \text{CF}_3
\end{align*}
Problem 2 - Total synthesis: missing reaction conditions

a) For the synthesis, please provide reasonable reaction conditions.

b) Please provide also the chemicals structure of the intermediate resulting from step vi.
**Problem 3 - Metal catalysis: mechanism**

a) For the reaction, please provide a reasonable mechanism. ([CITPPAI][Co(CO)$_4$]) is categorized as a bimetallic Lewis acid/nucleophilic metal carbonyl anion. A cobalt–acyl species should be considered among the key intermediates in the catalytic cycle.

b) Provide a rational for the recorded regioselectivity.
Problem 4 - Total synthesis: missing reagents

(a) In the multi-step synthesis, please provide reasonable chemical intermediates based on the given experimental reaction conditions.

(b) Please provide the structure of the (S,S)-Noyori catalyst for transfer hydrogenation;

(c) Please provide plausible TS for the final epoxidation step, accounting for the observed overall stereochemistry of E.

step ii: acetylene-zipper reaction