Supporting Information

Chiral Bis(imidazolinyl)phenyl NCN Pincer Rhodium(III) Catalysts for Enantioselective Allylation of Aldehydes and Carbonyl-Ene Reaction of Trifluoropyruvates

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The College of Chemistry and Molecular Engineering, Henan Key Laboratory of Chemical Biology and Organic Chemistry, Zhengzhou University, Zhengzhou 450052, People’s Republic of China

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Additional Catalytic Results

1. Allylation with allyltributyltin

\[
\begin{align*}
\text{F}_3\text{C} & \quad \text{O} & \quad \text{OEt} & \quad \text{+} & \quad \text{Sn}(\text{n-Bu})_3 \\
0.20 \text{ mmol} & \quad 0.30 \text{ mmol} & \quad \text{Rh-Phebim complex 1b (5 mol%) } & \quad \text{MS 4Å (250 mg) } & \quad \text{CH}_2\text{Cl}_2 (2 \text{ mL}, \text{rt, 6 h}) \\
\text{not detected}
\end{align*}
\]

\[
\begin{align*}
\text{F}_3\text{C} & \quad \text{O} & \quad \text{OEt} & \quad \text{+} & \quad \text{Sn}(\text{n-Bu})_3 \\
0.20 \text{ mmol} & \quad 0.30 \text{ mmol} & \quad \text{Rh-Phebim complex 1b (5 mol%) } & \quad \text{AgOTf (10 mol%), MS 4Å (250 mg) } & \quad \text{CH}_2\text{Cl}_2 (2 \text{ mL}, \text{rt, 6 h}) \\
\text{not detected}
\end{align*}
\]

\[
\begin{align*}
\text{H} & \quad \text{O} & \quad \text{OEt} & \quad \text{+} & \quad \text{Sn}(\text{n-Bu})_3 \\
0.20 \text{ mmol} & \quad 0.30 \text{ mmol} & \quad \text{Rh-Phebim complex 1b (5 mol%) } & \quad \text{MS 4Å (250 mg) } & \quad \text{CH}_2\text{Cl}_2 (2 \text{ mL}, \text{rt, 6 h}) \\
\text{not detected}
\end{align*}
\]

2. Carbonyl-Ene Reaction

\[
\begin{align*}
\text{Ph} & \quad \text{+} & \quad \text{PhCHO} \\
0.24 \text{ mmol} & \quad 0.20 \text{ mmol} & \quad \text{Rh-Phebim complex 1f (3 mol%) } & \quad \text{AgOTf (6 mol%) } & \quad \text{ClCH}_2\text{CH}_2\text{Cl (2 mL), rt, 16 h}} \\
\text{not detected}
\end{align*}
\]

\[
\begin{align*}
\text{Ph} & \quad \text{+} & \quad \text{HCOEt} \\
0.20 \text{ mmol} & \quad 0.40 \text{ mmol} & \quad \text{Rh-Phebim complex 1f (3 mol%) } & \quad \text{AgOTf (6 mol%) } & \quad \text{ClCH}_2\text{CH}_2\text{Cl (2 mL), rt, 16 h} \\
\text{70\% yield, 59\% ee}
\end{align*}
\]
### Peak NO. 1
- **Retention Time (Ret. Time):** 33.423 min
- **Peak Height:** 323795.563
- **Peak Area:** 31671792.000
- **Area %:** 49.9943

### Peak NO. 2
- **Retention Time (Ret. Time):** 40.240 min
- **Peak Height:** 265431.875
- **Peak Area:** 31679000.000
- **Area %:** 50.0057

### Peak NO. 1
- **Retention Time (Ret. Time):** 33.732 min
- **Peak Height:** 514781.594
- **Peak Area:** 34321036.000
- **Area %:** 79.7028

### Peak NO. 2
- **Retention Time (Ret. Time):** 40.240 min
- **Peak Height:** 136919.406
- **Peak Area:** 8740232.000
- **Area %:** 20.2972
(R)-Ethyl 2-hydroxy-4-phenylpent-4-enolate. Colorless oil (30.8 mg, 70%); The ee was determined on a Daicel Chiralcel OJ-H column with hexane/2-propanol = 100/1, flow = 1.0 mL/min, and detected at a UV wave length of 220 nm. Retention times: 33.7 min (major), 40.2 min, 59% ee. [α]_{D}^{20} = -52.9 (c 0.490, CH_{2}Cl_{2}). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): δ 7.43-7.41 (m, 2H), 7.36-7.32 (m, 2H), 7.30-7.27 (m, 1H), 5.40 (s, 1H), 5.21 (s, 1H), 4.29-4.25 (m, 1H), 4.16-4.08 (m, 1H), 4.07-3.99 (m, 1H), 3.09-3.04 (m, 1H), 2.87-2.82 (m, 1H), 2.71 (d, J = 6.3 Hz, 1H), 1.23 (t, J = 7.2 Hz, 3H).

Reference
Proposed Reaction Cycle for the Asymmetric Carbonyl-Ene Reaction: A catalytic cycle (Scheme S1, vide infra) for the carbonyl-ene reaction of trifluoropyruvates with alkenes using the NCN pincer Rh-Phebim complexes 1 is proposed based on the experimental results and literature reports.\textsuperscript{2} The reaction would be initiated by activation of complex 1 with AgOTf to form the dicationic complex I, which acts as an efficient Lewis acid catalyst. Chelate coordination of ethyl trifluoropyruvate 6a to the rhodium(III) center of I affords the intermediate II. Then Re-face attack of alkene 5 to the keto carbonyl group in II through the transition state A, followed by 1,5-sigma hydrogen migration results in the intermediate III, which subsequently undergoes decomplexation giving the desired product 7 and regenerating the active rhodium species I to fulfill the catalytic cycle.

References
Scheme S1. Proposed Reaction Cycle for the Asymmetric Carbonyl-Ene Reaction of Trifluoropyruvates Catalyzed by Pincer Rh-Phebim Complexes 1
Copies of the $^1$H, and $^{13}$C NMR Spectra of the Complex 1f
Copies of the NMR Spectra of the Compounds 4a-x
\text{OH}

\text{4v}

\text{OH}

\text{4w}
Copies of the NMR Spectra of the Compounds 7a-q
Br

COOEt

CF₃

OH

7j

1H

19F

CDCl₃

3167/SNP

160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

Br

COOEt

CF₃

OH

7j

1H

19F

CDCl₃

3167/SNP

0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 ppm
HPLC Spectra of the Compounds 4a-x

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## Peak NO. Ret. Time Peak Height Peak Area Area%

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[Diagram of chemical compounds]
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1 | 30.790 | 10144.000 | 459012.188 | 49.9633 
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PeakNO. | Ret.Time | PeakHeight | PeakArea     | Area%  
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### Peak NO.  Ret. Time  Peak Height  Peak Area  Area%

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### Peak NO.  Ret. Time  Peak Height  Peak Area  Area%

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### Table 1: peak area analysis

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![Graph 1](image1.png)

![Graph 2](image2.png)
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HPLC Spectra of the Compounds 7a-q

PeakNO. Ret.Time PeakHeight PeakArea Area%
1 12.923 306273.906 10372769.000 50.7050
2 17.598 225444.672 10084306.000 49.2950

PeakNO. Ret.Time PeakHeight PeakArea Area%
1 12.873 579198.250 20700032.000 96.2893
2 17.582 19889.672 797723.188 3.7107
PeakNO. | Ret.Time | PeakHeight | PeakArea   | Area%  
--- | --- | --- | --- | ---  
1 | 12.190 | 800569.500 | 23640882.000 | 49.8519  
2 | 15.215 | 744574.625 | 26817852.000 | 50.1481  

PeakNO. | Ret.Time | PeakHeight | PeakArea   | Area%  
--- | --- | --- | --- | ---  
1 | 11.348 | 970998.688 | 33070192.000 | 88.6327  
2 | 15.198 | 98546.336 | 4241327.500 | 11.3673  

- S59 -
### Peak NO. | Ret. Time | Peak Height | Peak Area | Area %
---|---|---|---|---
1 | 9.665 | 345590.531 | 4980970.500 | 50.6823
2 | 11.165 | 309929.313 | 4846852.000 | 49.3177

| Peak NO. | Ret. Time | Peak Height | Peak Area | Area %
---|---|---|---|---
1 | 9.632 | 64398.043 | 794367.625 | 5.5871
2 | 11.065 | 844225.625 | 13423424.000 | 94.4129
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1 | 10.107 | 4820.610 | 284871.438 | 49.8326  
2 | 12.857 | 4420.665 | 286785.063 | 50.1674  

PeakNO. | Ret.Time | PeakHeight | PeakArea  | Area%  
---|-------|----------|---------|-------
1 | 10.090 | 16755.367 | 877133.000 | 13.0837  
2 | 12.773 | 99026.906 | 5826876.500 | 86.9163  

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PeakNO.  Ret.Time  PeakHeight  PeakArea  Area%
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