Total Synthesis of (−)-Mitrephorone A

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- Antimicrobial/antitumor agent isolated from *Mitrephora glabra*.
- Contains a fully substituted oxetane ring, which is a common motif in natural products and to which its cytotoxicity can be ascribed.
- Highly congested structure (tetrasubstituted cyclopropane, four quaternary centers, and five contiguous stereocenters) poses a unique challenge for total synthesis.
Retrosynthetic Analysis

\[ (-)-\text{mitrephorone A (1)} \]

\[ \text{enolonium synthon} \]

\[ \text{readily available} \]

\[ \text{Electrophile} \]

\[ \text{Nucleophile} \]
**Chemical Reaction Diagram**

- **Compound 23**: DIBAL-H, toluene, -78 °C - 0 °C, yields 89%
  - **Compound 24**: TESO

**Additional Reaction Steps**

- **Compound 23**: H, aqueous workup, yields **Compound 24**: CHO
<table>
<thead>
<tr>
<th>Reaction Step</th>
<th>Compound</th>
<th>Conditions</th>
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</thead>
<tbody>
<tr>
<td>33 → 34</td>
<td></td>
<td>Et₂AlCN, toluene</td>
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<tr>
<td>34 → 36</td>
<td></td>
<td>H₂PO₄⁻/Pt(II), EtOH/H₂O</td>
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<tr>
<td>36 → 37</td>
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<td>KOH</td>
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**Yields and Diastereomeric Ratio (dr):**
- 33 → 34: 76%, dr = 7.8:1
- 36 → 37: 79%