Enantioselective Cyclization by a Hexacoordinated Chiral Hydrogen Phosphate

**Significance:** The Ooi group reports a Pictet–Spengler-type cyclization catalyzed by the Bronsted acid $\text{1} \cdot \text{H}$. The presented chiral hexacoordinated phosphate ion consists of two N,N,O-tridentate backbones, including 1,2-diphenylethylene-diamine as a readily available chiral source. The catalyst is prepared by deprotonation of a phenol followed by cation exchange. The authors obtained a single-crystal X-ray structure of $\text{1} \cdot \text{HNEt}_3$ which confirmed its octahedral P(V) core.

**Comment:** The authors demonstrate the catalytic activity of 1 as hydrogen phosphate. Although the substrate scope is limited, it is noteworthy that the hexacoordinated phosphate can indeed control the enantioselectivity. More mechanistic studies and control experiments would be highly appreciated to further understand and expand the presented transformation.

**Selected examples:**

- $R^1 = \text{Me, OMe, Cl}$
  - 88% yield, $\text{er} = 93.5:6.5$

- $R^2 = \text{Alk}$
  - 99% yield, $\text{er} = 95.5$
  - 96% yield, $\text{er} = 98.2$

**Catalyst synthesis:**

- 1. $\text{Na}_2\text{CO}_3$, H$_2$O–EtOAc
- 2. Amberlite IR-120 (Ag$^+$ form), Me$_2$S
- 3. t-BuCl, urea MeOH

$\text{1} \cdot \text{H}(\text{urea})_2$ (2 mol%) CH$_2$Cl$_2$ –90 °C

9 examples 87–99% yield $\text{er}$ from 93.5:6.5 to 98:2

$R^3 = 3.5$-Ph$_2$C$_6$H$_4$CH$_2$ 1 M