Highly Enantioselective Addition of Allyltrimethylsilane to Aldehydes

**Significance:** List and co-workers report the first general, highly enantioselective, organocatalytic addition of allyltrimethylsilane to aldehydes (the Hosomi–Sakurai reaction). This transformation is enabled by newly developed highly confined imidodiphosphorimidates \( \text{IDPi} \). Various aromatic and aliphatic aldehydes are tolerated under the reaction conditions, affording the desired products in good to excellent yields and enantioselectivities (er ≤ 98:2).

**Comment:** The IDPi motif, which can be accessed by a single-flask synthesis from 3,3'-disubstituted BINOL derivatives, is a combination of the recently developed highly confined imidodiphosphates (*Nature* 2012, 483, 315) and highly acidic BINOL-derived phosphoramidimides (*Synlett* 2016, 27, 156).

**Selected examples:**

- 92% yield er = 96:4
- 92% yield er = 92.5:7.5
- 70% yield er = 95.5:4.5
- 73% yield er = 96:4

\[
\text{IDPi} (0.05-2 \text{ mol%}) \quad \text{CH}_2\text{Cl}_2 \text{ or MePh} \quad -78 ^\circ \text{C} \quad \text{then aq HCl (1 M)}
\]

**Key words**
- silylium Lewis acids
- Hosomi–Sakurai reaction
- aldehydes
- allyltrimethylsilane
- imidodiphosphorimidates
- asymmetric catalysis

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