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Chiral Tin Dibromide Catalyzed Enantioselective N-Nitroso Aldol Reaction

**Significance:** A tin dibromide catalyzed enantioselective N-nitroso aldol reaction is reported. While organocatalysis and Lewis acid catalysis have been employed in asymmetric variants of this reaction, the reported method confers stereoinduction via a chiral metal enolate intermediate. Good yields and high ee values were generally achieved.

**Comment:** The developed method is selective for the N-nitroso aldol, whereas the competing O-nitroso aldol reactivity has also been reported in literature. The active catalyst in the reaction is the tin alkoxide species, which catalyzes the opening of the γ,δ-unsaturated δ-lactones to generate chiral tin enolates. The reaction can also give tertiary hydroxylamine with high yield and ee. However, steric bulk ortho to the nitroso group is required to afford efficient reactions and selectivity. Changing the ring size to the five-membered β,γ-unsaturated γ-butyrolactone also conferred reactivity, albeit with decreased yield and ee.

**Selected examples:**

1. Ph
   - 27% yield
   - 49% ee

2. 99% yield
   - 90% ee

3. (S)-3
   - 73% yield
   - 96% ee

**Equation:**

\[
\text{catalyst (10 mol\%) } \quad \text{NaOEt (10 mol\%)} \quad \text{EtOH (30 equiv)} \\
\text{THF or PhMe, 0 °C, 15 h} \quad \text{0.5 mmol scale} \\
\text{23–99% yield} \quad \text{38–99% ee}
\]