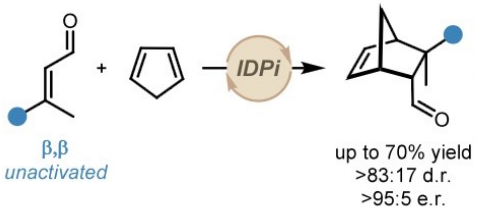
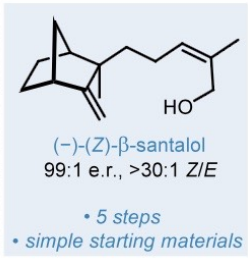
Catalytic Asymmetric Diels–Alder Reaction of β,β-Disubstituted Enals with Cyclopentadiene: Syntheses of (−)-Camphene, (−)-β-Santalene, and (−)-(Z)-β-Santalol

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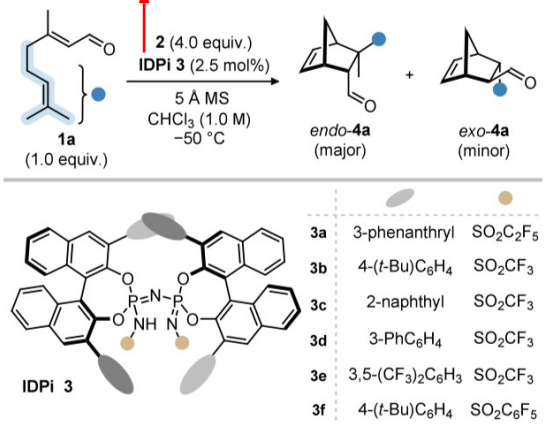
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- Steric congestion, hyperconjugation of the β-alkyl substituents, prone to selfcondensation and polymerization
- establishing up to four stereocenters, including one quaternary stereocenter

highly acidic and confined imidodiphosphorimidate (IDPi) catalysts



entry[a]	catalyst	yield (%)[b]	*endo*/*exo*	e.r. (*endo*)[c]
1	**3a**	15	87:13	73:27
2	**3b**	21	90:10	98:2
3	**3c**	9	85:15	77:23
4	**3d**	12	77:23	73:27
5	**3e**	24	60:40	69:31
6	**3f**	27	89:11	95:5
7[d]	**3f**	41	88:12	99:1
7[e]	**3f**	50	89:11	99:1
7[f]	**3f**	59	88:12	99:1

[a]0.05 mmol scale. [b]Yields and *endo*/*exo* ratios were determined via ^{1}H NMR using CH_2Br_2 as an internal standard. [c]Determined by chiral GC. [d]In MTBE (1.0 M). [e]In MTBE (1.0 M), **2** added before **1a**. [f]In MTBE (1.7 M), **2** added first, −40 °C. MS = molecular sieves. See SI, Chapter 2.2 for the details.

Recovery tests of MS and **3f**

Recovered 5 Å MS			
Run	1	2	3
Yield **4a**, %	67	60	58
e.r.	99:1		

Recovered **3f**			
Run	1	2	3
Yield **4a**, %	63	59	65
e.r.	99:1		

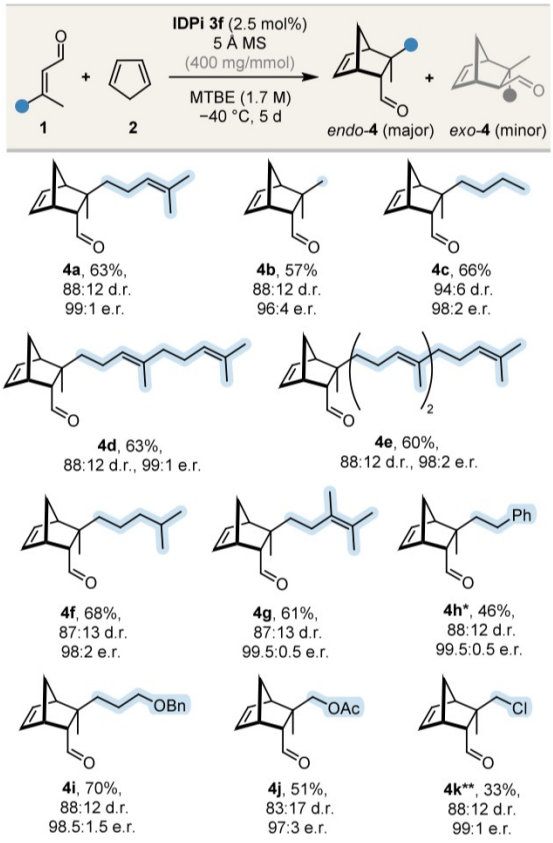


Figure 2. Substrate scope, 0.2 mmol scale. Isolated yields after chromatographic purification. Enantiomeric ratios for the major (*endo*) isomer are reported. *7 days, **at −60 °C.

simultaneous elongation of both β,β-substituents: unsuccess

switching to less reactive dienes: unsuccess

