

bined organic layers were dried (Na_2SO_4), the solvent was removed, and the crude residue was purified by chromatography (hexane/EtOAc 8:1 to 1:1) to give the product as a white solid; yield: 82%; 95% ee.

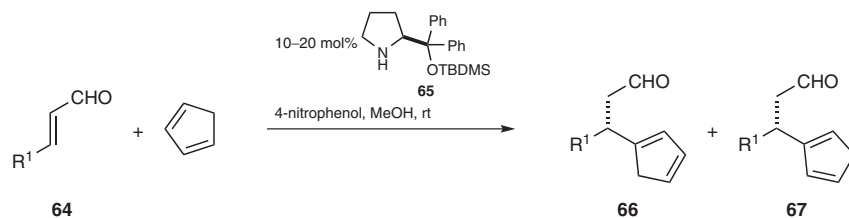
3.6.2.3 Electron-Deficient Alkenes as Enophiles

3.6.2.3.1 Enantioselective Reactions

3.6.2.3.1.1 Unactivated Alkenes as Ene Components

Although the enantioselective intermolecular carbonyl-ene reaction has been extensively investigated, the enantioselective ene reaction with electron-deficient alkenes as the enophile has received limited attention even taking into account the intramolecular variant.^[105,106] The first catalytic enantioselective intermolecular reaction^[107] emerged during the development of the enantioselective Diels–Alder reaction, using α,β -unsaturated aldehydes **64** with cyclopentadiene as the ene component. In this intriguing process diphenylprolinol silyl ether **65**^[108,109] proved to be an outstanding organocatalyst in the presence of 4-nitrophenol, affording the ene adducts in an efficient and highly enantioselective manner, albeit as a mixture of diene regioisomers **66** and **67** (Scheme 25). Interestingly, the 4-nitrophenol is critical for the success of the reaction, since other strong acids, such as trifluoroacetic acid and hydrogen chloride are unsuccessful.

Scheme 25 Enantioselective Ene Reaction of α,β -Unsaturated Aldehydes with Cyclopentadiene Catalyzed by a Diphenylprolinol Silyl Ether^[107]



R ¹	Catalyst 65 (mol%)	Time (h)	Ratio (66/67)	ee ^a (%)	Yield (%)	Ref
Ph	10	20	70:30	92	84	[107]
2-naphthyl	20	3	57:43	93	70	[107]
4-O ₂ NC ₆ H ₄	20	3	43:57	90	60 ^b	[107]
4-BrC ₆ H ₄	20	6	67:33	95	79	[107]
4-MeOC ₆ H ₄	10	8	57:43	93	82	[107]
	10	5	60:40	93	78	[107]
2-furyl	20	2	63:37	91	80	[107]
2-thienyl	10	3	40:60	77	82	[107]
2-MeOC ₆ H ₄	20	3	82:18	95	80	[107]

^a Determined after reduction and hydrogenation.

^b Diels–Alder products are obtained in 11% yield.