Supporting Information
for
N-Heterocyclic carbene catalyzed transformylation

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I. General experimental

Proton (1H) and carbon (13C) NMR spectra were recorded on a Varian Mercury 500 spectrometer operating at 500 MHz for proton, a Bruker DRX600 spectrometer operating at 150 MHz for carbon nuclei, a Bruker DRX400 spectrometer operating at 400 MHz for proton and 100 MHz for carbon nuclei, and a Bruker DRX300 spectrometer operating at 300 MHz for proton and 75 MHz for carbon nuclei. 2D correlation spectra were recorded on a Bruker DRX400 spectrometer. Infrared spectra (νmax) were recorded on an Agilent Cary 630 FTIR Spectrometer. High resolution mass spectra (HRMS) (ESI) were recorded on a Bruker BioApex 47e FTMS fitted with an Analytical electrospray source using NaI for accurate mass calibration.

Analytical chiral HPLC was performed with a Perkin Elmer Series 200 HPLC using either a Chiralpak AD-H or OJ-H (4.6 mm x 25 cm) obtained from Daicel Chemical Industries, Ltd. with visualization at 238 nm.

Flash column chromatography was performed on silica gel (Davisol LC60A, 40-63 μm silica media) using compressed air. Thin layer chromatography (TLC) was performed using aluminum-backed plates coated with 0.2 mm silica (Merck, DC-Platten, Kieselgel; 60 F254 plates). Eluted plates were visualized using a 254 nm UV lamp and/or by treatment with a suitable stain followed by heating.

Starting materials and reagents were purchased from Sigma-Aldrich or Oakwood and were used as supplied or, in the case of some liquids, distilled. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl and acetonitrile (CH3CN) and dichloromethane (CH2Cl2) were dried by passing over activated alumina. Unless otherwise stated, all reactions were conducted in flame-dried glassware under a N2 atmosphere.

NHC precatalysts IMes.HCl (A1-HCl), A2-HBF4, A3-HCl and B1-HClO4 were prepared according to literature procedures.1

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4-Phenylbutyl formate (5e)
2,4-Dimethoxybenzyl formate (5g)
4-Methoxyphenethyl formate (5h)
Cinnamyl formate (5i)
(2-(4-Methoxyphenyl)cyclopropyl)methyl formate (5j)
(Tetrahydrofuran-2-yl)methyl formate (5k)
Furan-2-ylmethyl formate (5l)
**tert-Butyl 2-((formyloxy)methyl)-1H-pyrrole-1-carboxylate (5m)**

![Chemical Structure](image)
3-((tert-Butyldimethylsilyl)oxy)-2,2-dimethylpropyl formate (5n)
2-((tert-Butoxycarbonyl)amino)-3-methylbutyl formate \((5o)\)

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\begin{align*}
\text{H}_3C & \quad \text{O} \quad \text{O} \\
\text{CH}_3 & \quad \text{NHBoc}
\end{align*}
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(S)-1-Phenylethyl formate (5p)

HPLC (S)-1-Phenylethyl formate (5p)
Dihydrocholesterol derived formate (5v)