Nickel-Catalyzed Asymmetric Transfer Hydrogenation of Conjugated Olefins

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Supporting Information: Procedures and Characterization

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I. General

All NMR spectra were acquired on Bruker AV 500 MHz or 300 MHz NMR spectrometers. $^1$H NMR (500 MHz) chemical shifts were recorded relative to SiMe$_4$ ($\delta$ 0.00) or residual protiated solvents (CDCl$_3$: $\delta$ 7.26). Multiplicities were given as: s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet). The number of protons (n) for a given resonance was indicated by nH. Coupling constants were reported as a $J$ value in Hz. $^{13}$C NMR (125 MHz) chemical shifts were recorded relative to solvent resonance (CDCl$_3$: $\delta$ 77.16).

Glassware was dried at 120 °C for at least 3 h before use. Dry THF was freshly distilled from sodium/benzophenone under argon before use. Anhydrous 1,4-dioxane (Aldrich) was stored over activated 4 Å molecular sieve beads in an argon-filled glove box. Dry toluene was collected from a solvent purification system containing a column of activated alumina (1 m x 2) under argon. Methanol, ethanol and isopropanol were degassed and stored over dried molecular sieve in an argon-filled glove box before use. All anhydrous solvents were stored in Schlenk tubes in the glove box.

Unless noted otherwise, commercially available chemicals were used as received without purification. The GC internal standard, $n$-C$_{12}$H$_{26}$ and $n$-C$_{14}$H$_{30}$ was degassed with argon and dried over activated 4 Å molecular sieve beads before use. Flash chromatography was performed using Merck 40-63D 60 Å silica gel. Gas chromatography (GC) analysis was performed on a Shimadzu GC-2010 instrument with Agilent J & W GCcolumn DB-5MS-UI. GC/MS analysis was conducted on a Thermo Scientific DSQ II single quadrupole GC/MS instrument with Agilent J & W GC column DB-5MS-UI. ESI/MS analysis was conducted on a ThermoFinnigan LCQ Fleet MS spectrometer. Chiral HPLC analysis was performed on a Shimadzu LC-20AD instrument using Daicel Chiracel columns at 25°C and a mixture of HPLC-grade hexanes and isopropanol as eluent. Optical rotation was measured using a JASCO P-1030 Polarimeter equipped with a sodium vapor lamp at 589 nm and the concentration of samples was denoted as $c$. 
II. Condition optimization for asymmetric transfer hydrogenation

A typical procedure for condition optimization: In an argon-filled glove box, NiBr₂(DME) (1.2 mg, 0.004 mmol), (R)-Me-DuPhos (1.5 mg, 0.0048 mmol) and dry isopropanol (0.3 mL) were charged into a 10-mL reaction tube. After stirring for 10 min, dry Et₃N (28 µL, 0.2 mmol), formic acid (19 µL, 0.5 mmol), (E)-ethyl 3-methylcinnamate (20 mg, 0.1 mmol) and GC standard n-C₁₂H₂₆ (10 µL) were added. The reaction mixture was heated with stirring in an oil bath maintained at 80 °C. Aliquots were taken from the reaction mixture after sometime in the glove box and passed through a short plug of silica gel with Et₂O washing (about 3 mL). The filtrate was subjected to GC analysis to determine the conversion of the olefin and yield of the product.

To determine the enantioselectivity of product, the filtered sample was subjected to chiral HPLC analysis (Daicel CHIRCEL OD-H; 2% iPrOH in hexanes; flow rate 0.5 mL/min). The racemic product was prepared by hydrogenation with hydrogen gas (8 bar) over 10% Pd/C in methanol at room temperature.

Table S1. The effect of organic solvents

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<th>Conversion (%)</th>
<th>Yield (%)</th>
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<td><strong>90</strong></td>
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<td>i-PrOH</td>
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<td>Diglyme</td>
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**Table S2.** The effect of metal salts

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<td>Ni(OTf)₂</td>
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<td>Ni(acac)₂</td>
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**Table S3.** Effect of formic acid and Et₃N ratio

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<th>Et₃N (equiv)</th>
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<td>Structure 3</td>
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III. Procedures for asymmetric transfer hydrogenation

A general procedure: In an argon-filled glove box, NiBr$_2$(DME) (6.0 mg, 0.02 mmol), (R)-Me-DuPhos (7.5 mg, 0.024 mmol) and dry i-PrOH (1.5 mL) were charged into a dry 10-mL Schlenk tube. After stirring for 10 min at room temperature, dry Et$_3$N (140 μL, 1.0 mmol, 2 equiv), formic acid (95 μL, 2.5 mmol, 5 equiv), olefin (0.5 mmol) were added. The reaction mixture was heated with vigorous stirring in an oil bath maintained at 80 °C, until the olefin was fully or almost fully consumed as monitored by GC. After the reaction mixture was cooled to room temperature, solid NaHCO$_3$ was added to basify the mixture. After evaporation of the solvent on a rotary evaporator, the residue was purified by flash chromatography using ethyl acetate and hexanes as eluent. The enantioselectivity (ee) of the purified product was determined by chiral HPLC analysis with Daicel Chiralcel columns. The reaction scale of 0.5 mmol was used unless stated otherwise. The use of Schlenk tubes and a vacuum manifold instead of a glove box gave similar results.
(S)-Methyl 3-phenylbutanoate [1441-20-9]. Methyl (E)-3-phenylcrotonate (88 mg, 0.5 mmol) were used. The reaction was complete after 24 h at 80 °C. The product was isolated by flash chromatography (Et₂O/hexanes 1:20) as colorless oil. Yield: 82 mg, 92%.

\[ \alpha^2_\mathrm{D} = 19.7^\circ \ (c = 0.94, \text{CHCl}_3). \]

Ee: 94%. Daicel Chiralcel OD-H, n-hexane/isopropanol 98/2, flow rate = 0.5 mL/min.

\[ \begin{array}{ccc}
\text{Peak} & \text{Ret. Time} & \text{Area} \\
1 & 11.095 & 10902752 \\
2 & 23.166 & 10902752 \\
\text{Total} & & 10902752 \\
\end{array} \]

\[ \begin{array}{ccc}
\text{Peak} & \text{Ret. Time} & \text{Area} \\
1 & 22.963 & 24647616 \\
\text{Total} & & 24647616 \\
\end{array} \]

\[ \begin{array}{ccc}
\text{Peak} & \text{Ret. Time} & \text{Area} \\
1 & 11.137 & 495247 \\
\text{Total} & & 495247 \\
\end{array} \]

\[ \begin{array}{ccc}
\text{Peak} & \text{Ret. Time} & \text{Area} \\
1 & 22.963 & 24647616 \\
\text{Total} & & 24647616 \\
\end{array} \]

\[ \begin{array}{ccc}
\text{Peak} & \text{Ret. Time} & \text{Area} \\
1 & 22.963 & 24647616 \\
\text{Total} & & 24647616 \\
\end{array} \]

H NMR (300 MHz, CDCl₃): \( \delta \) 7.36-7.16 (m, 5H), 3.62 (s, 3H), 3.36-3.20 (m, 1H), 2.69-2.49 (m, 2H), 1.30 (d, \( J = 7.0 \) Hz, 3H).

\[ 1^3 \text{C NMR (100 MHz, CDCl}_3\) \( \delta \) 172.9, 145.7, 128.5, 126.7, 126.4, 51.5, 42.8, 36.5, 21.8. \]


(\( \text{S} \))-Ethyl 3-phenylbutanoate [1134-71-0]. Ethyl (E)-3-phenyl-2-butenoate (95 mg, 0.5 mmol) were used. The reaction was complete after 24 h at 80 °C. The product was isolated by flash chromatography (Et₂O/hexanes 1:20) as colorless oil. Yield: 88 mg, 92%.

\[ \alpha^2_\mathrm{D} = 25.1^\circ \ (c = 0.95, \text{CHCl}_3). \]

91% ee. Daicel Chiralcel OD-H, n-hexane/isopropanol 98/2, flow rate = 0.5 mL/min.
$^1$H NMR (300 MHz, CDCl₃): δ 7.41-7.09 (m, 5H), 4.08 (q, $J = 7.1$ Hz, 2H), 3.47-3.18 (m, 1H), 2.67-2.47 (m, 2H), 1.3 (d, $J = 7.0$ Hz, 3H), 1.18 (t, $J = 7.1$ Hz, 3H).

$^{13}$C NMR (125 MHz, CDCl₃) δ 172.4, 145.8, 128.5, 126.8, 126.4, 60.3, 43.0, 36.5, 21.8, 14.2.


A gram-scale transfer hydrogenation for isolation: Under argon, NiBr₂(DME) (30 mg, 0.1 mmol, 2 mol%), (R)-Me-DuPhos (38 mg, 0.12 mmol, 2.4 mol%) and dry diglyme (5 mL) were charged into a dry 50-mL Schlenk tube. After stirring for 15 min at room temperature, dry Et₃N (1.4 mL, 10 mmol, 2 equiv), formic acid (0.95 mL, 25 mmol, 5 equiv), ethyl (E)-3-phenylcrotonate (0.95 g, 5 mmol) were added. The reaction mixture was heated with vigorous stirring in an oil bath maintained at 90 °C for 3 days until almost full conversion, as monitored by GC. After the reaction mixture was cooled to room temperature, solid NaHCO₃ was added to basify the mixture. After workup and flash chromatography, the product was isolated as colorless oil. 881 mg, 92% yield. 90% ee. If isopropanol was used as the solvent, lower conversion was seen.

(S)-$t$-Butyl 3-phenylbutanoate [67217-41-8]. $t$-Butyl (E)-3-phenyl-2-butenoate (109 mg, 0.5 mmol) were used. The reaction was complete after 24 h at 80 °C. The product was isolated by flash chromatography (Et₂O/hexanes 1:20) as colorless oil. Yield: 102 mg, 93%.

[$\alpha$]²³ D = 27.3° ($c = 0.80$, CHCl₃).

Ee: 88%. Daicel Chiralcel OD-H, n-hexane/isopropanol 99.5/0.5, flow rate = 0.5 mL/min.
\(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 7.29-7.14 (m, 5H), 3.31-3.14 (m, 1H), 2.60-2.36 (m, 2H), 1.35 (s, 9H), 1.29 (d, \(J = 7.0\) Hz, 3H).

GC-MS (EI): Calcd for C\(_{14}\)H\(_{20}\)O\(_2\): 220.15. Found: 220.0.

\(\text{(S)}\)-Ethyl 3-phenylpentanoate [2845-23-0]. \((E)\)-Ethyl 3-phenyl-2-pentenoate (102 mg, 0.5 mmol) were used. The reaction completed after 36 h at 80 °C. The product was isolated by flash chromatography (Et\(_2\)O/hexanes 1:20) as colorless oil. Yield: 91 mg, 88%.

\([\alpha]^{23}_D = 14.3^\circ\) \((c = 0.91, \text{CHCl}_3)\).

Ec: 92%. Daicel Chiralcel OD-H, \(n\)-hexane/isopropanol 99/1, flow rate = 0.5 mL/min.
\[ ^1\text{H NMR } (300 \text{ MHz, CDCl}_3): \delta 7.39-7.16 \text{ (m, 5H)}, 4.03 \text{ (q, } J = 7.1 \text{ Hz, 2H)}, 3.07-2.93 \text{ (m, 1H), 2.69-2.48 \text{ (m, 2H), 1.80-1.50 \text{ (m, 2H), 1.13 \text{ (t, } J = 7.1 \text{ Hz, 3H), 0.79 \text{ (t, } J = 7.4 \text{ Hz, 3H). }}\]

\[ ^{13}\text{C NMR } (100 \text{ MHz, CDCl}_3) \delta 172.53, 143.93, 128.34, 127.56, 126.38, 60.19, 43.97, 41.52, 29.14, 14.12, 11.91. \]

GC-MS (EI): Calcd for \( C_{13}H_{18}O_2 \): 206.1. Found: 206.0.

**\((S)\)-Ethyl 3-(4-tolyl)butanoate [1461-11-6].** \((E)\)-Ethyl 3-(4-tolyl)-2-butenoate (102 mg, 0.5 mmol) were used. The reaction completed after 24 h at 80 °C. The product was isolated by flash chromatography (Et\(_2\)O/hexanes 1:20) as colorless oil. Yield: 96 mg, 93%.

\([\alpha]_D^{23} = 26.4^\circ \hspace{1em} (c = 0.91, \text{ CHCl}_3). \]

Ee: 92%. Daicel Chiralcel OJ-H, n-hexane/isopropanol 99/1, flow rate = 0.5 mL/min.

\[ ^1\text{H NMR } (300 \text{ MHz, CDCl}_3): \delta 7.13-7.10 \text{ (m, 4H), 4.08 \text{ (q, } J = 7.1 \text{ Hz, 2H), 3.38-3.12 \text{ (m, 1H), 2.67-2.48 \text{ (m, 2H), 2.31 \text{ (s, 3H), 1.28 \text{ (d, } J = 7.0 \text{ Hz, 3H), 1.19 \text{ (t, } J = 7.1 \text{ Hz, 3H).}}\]

\[ ^{13}\text{C NMR } (125 \text{ MHz, CDCl}_3) \delta 172.5, 142.8, 135.8, 129.2, 126.6, 60.2, 43.1, 36.1, 21.9, 21.0, 14.2. \]

GC-MS (EI): Calcd for \( C_{13}H_{18}O_2 \): 206.1. Found: 205.9.
(S)-Ethyl 3-(4-anisyl)butanoate [1242409-36-4]. (E)-Ethyl 3-(4-anisyl)-2-butoenate (110 mg, 0.5 mmol) were used. The reaction completed after 24 h at 80 °C. The product was isolated by flash chromatography (Et₂O/hexanes 1:20) as colorless oil. Yield: 104 mg, 94%.

\[ \alpha \]²³ D = 26.2° (c = 0.94, CHCl₃).

Ee: 92%. Daicel Chiralcel OJ-H, n-hexane/isopropanol 99.5/0.5, flow rate = 0.5 mL/min.

\[^1\text{H} \text{NMR (300 MHz, CDCl}_3\text{): } \delta 7.16-7.12 \text{ (m, 2H), 6.86-6.81 (m, 2H), 4.07 (q, J = 7.1 Hz, 2H), 3.78 (s, 3H), 3.37-3.14 (m, 1H), 2.71-2.38 (m, 2H), 1.27 (d, J = 7.0 Hz, 3H), 1.18 (t, J = 7.1 Hz, 3H).} \]

\[^{13}\text{C} \text{NMR (100 MHz, CDCl}_3\text{): } \delta 172.4, 158.1, 137.9, 127.7, 113.9, 60.2, 55.3, 43.3, 35.8, 22.0, 14.2. \]

GC-MS (EI): Calcd for C₁₃H₁₈O₃: 222.1. Found: 222.0.

(S)-Ethyl 3-(o-anisyl)butanoate [128950-12-9]. (E)-Ethyl 3-(o-anisyl)but-2-enoate (110 mg, 0.5 mmol), formic acid (10 equiv) and Et₃N (4 equiv) were used. The reaction completed after 48 h at 80 °C. The product was isolated by flash chromatography (Et₂O/hexanes 1:30) as colorless oil.
82% yield, 89 mg. If a 5:2 mixture of formic acid and Et₃N was used, 71% conversion at 24 hours at 80 °C.

Ee: 80%. Daicel Chiralcel IC-H, n-hexane/isopropanol 98/2, flow rate = 0.5 mL/min.

\[ \text{Ee: 80%. Daicel Chiralcel IC-H, } n\text{-hexane/isopropanol 98/2, flow rate = 0.5 mL/min.} \]

1H NMR (500 MHz, CDCl₃): \( \delta \) 7.21-7.16 (m, 2H), 6.91 (\( \gamma \)td, \( J = 7.5, 1.0 \text{ Hz, 1H} \)), 6.85 (d, \( J = 8.1 \text{ Hz, 1H} \)), 4.09 (q, \( J = 7.1 \text{ Hz, 2H} \)), 3.83 (s, 3H), 3.72-3.58 (m, 1H), 2.68 (dd, \( J = 15.0, 6.0 \text{ Hz 1H} \)), 2.50 (dd, \( J = 15.0, 8.9 \text{ Hz 1H} \)), 1.28 (d, \( J = 7.0 \text{ Hz, 3H} \)), 1.20 (d, \( J = 7.1 \text{ Hz, 3H} \)).


\[ \text{(S)-Ethyl 3-}(m\text{-tolyl})\text{butanoate[130378-45-9]. (E)-Ethyl 3-}(m\text{-tolyl})\text{but-2-enoate (102 mg, 0.5 mmol) were used. The reaction completed after 24 h at 80 °C. The product was isolated by flash chromatography (Et₂O/hexanes 1:30) as colorless oil. Yield: 91 mg, 88%.} \]

\[ [\alpha]_{D}^{23} = 22.0 (c = 0.91, \text{ CHCl}_3). \]

Ee: 94%. Daicel Chiralcel OD-H, n-hexane/isopropanol 90/10, flow rate = 0.5 mL/min.
\( ^1\)H NMR (300 MHz, CDCl\(_3\)): \( \delta \) 7.21-7.16 (m, 1H), 7.03-7.01 (m, 3H), 4.09 (q, \( J = 7.1 \) Hz, 2H), 3.37-3.12 (m, 1H), 2.63-2.33 (m, 2H), 2.33 (s, 3H), 1.29 (d, \( J = 6.9 \) Hz, 3H), 1.19 (t, \( J = 7.1 \) Hz, 3H).

\( ^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 172.5, 145.8, 138.0, 128.4, 127.6, 127.1, 123.7, 60.2, 43.0, 36.5, 21.8, 21.5, 14.2.

MS (ESI): Calcd for C\(_{13}\)H\(_{19}\)O\(_2\) [M+1]: 207.1. Found: 206.8.

(S)-Ethyl 3-(2-naphthyl)butanoate [52086-00-7]. (E)-Ethyl 3-(2-naphthyl)-2-butenoate (120 mg, 0.5 mmol) were used. The reaction completed after 24 h at 80 °C. The product was isolated by flash chromatography (Et\(_2\)O/hexanes 1:20) as colorless oil. Yield: 111 mg, 92%.

\([\alpha]^{23}_D = 25.1^\circ \) (c = 0.91, CHCl\(_3\)).

Ee: 91%. Daicel Chiralcel OJ-H, n-hexane/isopropanol 95/5, flow rate = 0.5 mL/min.
\( ^1H \) NMR (300 MHz, CDCl\(_3\)): \( \delta \) 7.81-7.78 (m, 3H), \( \delta \) 7.66 (s, 1H), \( \delta \) 7.48-7.26 (m, 3H), 4.07 (q, \( J = 7.0 \) Hz, 2H), 3.54-3.34 (m, 1H), 2.78-2.56 (m, 2H), 1.39 (d, \( J = 7.0 \) Hz, 3H), 1.17 (t, \( J = 7.0 \) Hz, 3H).

\( ^13C \) NMR (100 MHz, CDCl\(_3\)): \( \delta \) 172.4, 143.2, 133.6, 132.4, 128.2, 127.7, 127.6, 126.0, 125.6, 125.4, 125.0, 60.3, 43.0, 36.7, 21.9, 14.2.


\( (S)\)-Ethyl 3-(2-thienyl)butanoate [27050-13-1]. \( (E)\)-Ethyl 3-(2-thienyl)-2-butenoate (120 mg, 0.5 mmol) were used. The reaction completed after 24 h at 80 °C. The product was isolated by flash chromatography (Et\(_2\)O/hexanes 1:20) as colorless oil. Yield: 90 mg, 91%.

\([\alpha]^{23}_D = 17.6^\circ \) (c = 0.80, CHCl\(_3\)).

Ee: 89% ee. Daicel Chiralcel OD-H, n-hexane/isopropanol 99.5/0.5, flow rate = 0.5 mL/min.
(S)-Ethyl 3-(3-pyridyl)butanoate [71351-56-9]. (E)-Ethyl 3-(3-pyridyl)-2-butenoate (96 mg, 0.5 mmol) were used. The reaction completed after 36 h at 80 °C. The product was isolated by flash chromatography (Et₂O/hexanes 1:20) as colorless oil. Yield: 90 mg, 92%.

\[ \alpha^D_{23} = 21.9^\circ \ (c = 0.99, \text{CHCl}_3) \]

Ee: 82%. Daicel Chiralcel AS-H, n-hexane/isopropanol 98/2, flow rate = 0.5 mL/min.

**1H NMR (300 MHz, CDCl₃):** δ 8.50 (d, J = 2.1 Hz, 1H), 8.45 (dd, J = 4.8, 1.6 Hz, 1H), 7.55-7.52 (m, 1H), 7.24-7.20 (m, 1H), 4.07 (q, J = 7.1 Hz, 2H), 3.37-3.23 (m, 1H), 2.64-2.54 (m, 2H), 1.32 (d, J = 7.0 Hz, 3H), 1.17 (t, J = 7.1 Hz, 3H).

**13C NMR (125 MHz, CDCl₃):** δ 171.8, 148.8, 147.9, 140.8, 134.2, 123.4, 60.5, 42.5, 34.1, 21.6, 14.1.

GC-MS (Ei): Calcd for C₁₁H₁₅NO₂: 193.1. Found: 194.0.

(S)-Ethyl 3-(4-trifluoromethylphenyl)butanoate. (E)-Ethyl 3-(4-trifluoromethylphenyl)-2-butenoate (129 mg, 0.5 mmol) were used. The reaction completed after 36 h at 80 °C. The product was isolated by flash chromatography (Et₂O/hexanes 1:20) as colorless oil. Yield: 120 mg, 92%.

\[ \alpha^D_{23} = 17.1^\circ \ (c = 1.09, \text{CHCl}_3) \]

Ee: 90%. Daicel Chiralcel IC-H, n-hexane/isopropanol 99.9/0.1, flow rate = 0.5 mL/min.
$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.56 (d, $J = 8.2$ Hz, 2H), 7.34 (d, $J = 8.2$, 2H), 4.07 (q, $J = 7.1$ Hz, 2H), 3.44-3.27 (m, 1H), 2.71-2.45 (m, 2H), 1.32 (d, $J = 7.0$ Hz, 3H), 1.17 (t, $J = 7.1$ Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 171.9, 149.76, 128.75 (q, $J = 32.4$ Hz), 127.2, 125.5 (q, $J = 3.7$ Hz), 124.2 (q, $J = 271.8$ Hz), 60.42, 42.55, 36.38, 21.71, 14.11

$^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -62.4.

GC-MS (EI): Calcd for C$_{13}$H$_{15}$F$_3$O$_2$: 260.1. Found: 260.0.

**$(S)$-Ethyl 2-(1-tetralinyl)acetate.** The (E)-isomer of starting material was used. The reaction completed after 24 h at 80 °C. The product was isolated by flash chromatography (Et$_2$O/hexanes 1:15) as colorless oil. Yield: 107 mg, 98%.

$[\alpha]^{23}_D = 1.2$ (c = 1, CHCl$_3$)

Ee: 94%. Daicel Chiralcel OJ-H, $n$-hexane/isopropanol 98/2, flow rate = 1.0 mL/min.
$^1$H NMR (500 MHz, CDCl$_3$): δ 7.25-6.78 (m, 4H), 4.17 (q, $J = 7.1$ Hz, 2H), 3.35 (m, 1H), 2.79-2.73 (m, 2H), 2.70 (dd, $J = 15.2, 4.8$ Hz, 1H), 2.52 (dd, $J = 15.2, 9.9$ Hz, 1H), 1.95-1.67 (m, 4H), 1.27 (t, $J = 7.1$ Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 172.9, 139.4, 137.2, 129.3, 128.3, 126.1, 125.9, 60.4, 42.1, 34.7, 29.6, 28.3, 19.7, 14.4.

MS (ESI): Calcd for C$_{14}$H$_{19}$O$_2$ [M+H]: 219.1. Found: 219.0

(S)-Ethyl 2-(4-chromanyl)acetate. The (E)-isomer of starting material was used. The reaction completed after 24 h at 80 °C. The product was isolated by flash chromatography (EtOAc/hexanes 1:4) as colorless oil. Yield: 108 mg, 98%.

$[\alpha]_{D}^{23} = 6.8$ (c = 1, CHCl$_3$)

Ee: 93%. Daicel Chiralcel OJ-H, n-hexane/isopropanol 90/10, flow rate = 1.0 mL/min.
\(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.12-7.07 (m, 2H), 6.88-6.82 (m, 1H), 6.79 (d, \(J = 8.1 \text{ Hz}, 1\)H), 4.20-4.13 (m, 4H), 3.35 (m, 1H), 2.78 (dd, \(J = 15.6, 4.7 \text{ Hz}, 1\)H), 2.51 (dd, \(J = 15.6, 10.0 \text{ Hz}, 1\)H), 2.16-2.12 (m, 1H), 1.83 (m, 1H), 1.27 (t, \(J = 7.2 \text{ Hz}, 3\)H).

\(^1\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 172.1, 154.6, 128.7, 127.8, 124.6, 120.4, 117.1, 63.2, 60.6, 41.4, 30.5, 27.4, 14.3.

MS (ESI): Calcd for C\(_{13}\)H\(_{17}\)O\(_3\) [M+H]: 221.1 Found: 221.0

(S)-3-Phenylbutyronitrile [211203-12-5]. (E)-3-Phenylbut-2-enenitrile (71 mg, 0.5 mmol) were used. The reaction completed after 24 h at 80 °C. The product was isolated by flash chromatography (Et\(_2\)O/hexanes 1:15) as colorless oil. Yield: 62 mg, 85%.

\([\alpha]^{23}_D = -2.81^\circ\) (c = 0.80, CHCl\(_3\)).

91% ee. Daicel Chiralcel OD-H, n-hexane/isopropanol 90/10, flow rate = 0.5 mL/min.

\(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 7.42-7.20 (m, 5H), 3.28-3.02 (m, 1H), 2.74-2.44 (m, 2H), 1.46 (d, \(J = 7.0 \text{ Hz}, 3\)H).
$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 143.2, 128.9, 127.4, 126.6, 118.6, 36.6, 26.4, 20.7.

MS (ESI): Calcd for C$_{10}$H$_{12}$N [M+H]: 146.2. Found: 146.0.

(S)-$N,N$-Diethyl 3-phenylbutyramide [857779-92-0]. $N,N$-diethyl (E)-3-methylcinnamide (110 mg, 0.5 mmol) were used. The reaction completed after 48 h at 80 °C. The product was isolated by flash chromatography (Ethyl acetate/hexanes 1:30) as colorless oil. Yield: 96 mg, 87%. 82% ee. Daicel Chiralcel OD-H, $n$-hexane/isopropanol 98/2, flow rate = 0.5 mL/min.

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.30-7.17 (m, 5H), 3.45-3.34 (m, 2H), 3.32-3.25 (m, 1H), 3.23-3.12 (m, 1H), 2.59-2.46 (m, 2H), 1.33 (d, $J$ = 7.0 Hz, 3H), 1.12-1.02 (m, 6H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 170.8, 146.6, 128.4, 126.9, 126.2, 41.9, 41.7, 40.2, 36.7, 21.4, 14.4, 13.0.

GC-MS (EI): Calcd for C$_{11}$H$_{15}$NO$_2$ M: 219.3. Found: 219.1.
(S)-Dimethyl 2-phenylsuccinate (E)-Dimethyl 2-phenylfumarate (110 mg, 0.5 mmol) was used.
NiBr₂(DME) (6.0 mg, 0.02 mmol), (S,S′,R,R′)-TangPhos (6.9 mg, 0.024 mmol) and dry toluene
(1.5 mL) were used. After stirring for 10 min at room temperature, Et₃N (140 μL, 1.0 mmol, 2
equiv), formic acid (95 μL, 2.5 mmol, 5 equiv) and (Z)-olefin (0.5 mmol) were added. The
reaction completed after 24 h at 60 °C. The product was isolated by flash chromatography
(Et₂O/hexanes 1:20) as colorless oil. Yield: 108 mg, 97%. When Me-DuPhos ligand was used in
i-PrOH at 80 °C, 65% ee was obtained.

[α]²³_D = 114.9° (c = 0.82, CHCl₃).

Ee: 94%. Daicel Chiralcel OJ-H, n-hexane/isopropanol 80/20, flow rate = 1.0 mL/min.

1H NMR (400 MHz, CDCl₃): δ 7.35-7.27 (m, 5H), 4.09 (dd, J = 10.1, 5.2 Hz, 1H), 3.68 (s, 3H),
3.67 (s, 3H), 3.28 (dd, J = 17.0, 10.1 Hz, 1H), 2.67 (dd, J = 17.0, 5.2 Hz, 1H).

13C NMR (100 MHz, CDCl₃) δ 173.4, 172.0, 137.7, 128.9, 127.7, 127.7, 52.3, 51.8, 47.1, 37.6.


(S)-Ethyl 3-benzylbutanoate [72277-22-6]. Ethyl (E)-3-benzyl-2-butenoate (102 mg, 0.5 mmol)
was used. The reaction was complete after 48 h at 80 °C. The product was isolated by flash
chromatography (Et₂O/hexanes 1:50) as colorless oil. Yield: 90 mg, 87%.

54% ee. Daicel Chiralcel OD-H, n-hexane/isopropanol 99.5/0.5, flow rate = 0.5 mL/min.
$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.33-7.24 (m, 2H), 7.22-7.13 (m, 3H), 4.11 (q, $J = 7.1$ Hz, 2H), 4.13-4.08 (m, 2H), 2.37-2.21 (m, 2H), 2.20-2.08 (m, 1H), 1.24 (t, $J = 7.1$ Hz, 3H), 0.94 (d, $J = 6.6$ Hz, 3H).

$^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 173.1, 140.3, 129.2, 128.3, 126.0, 60.2, 43.0, 41.2, 32.3, 19.6, 14.3.

GC-MS (EI): Calcd for C$_{13}$H$_{18}$O$_2$: 206.3. Found: 206.0.

The reaction was conducted using 0.1 mmol of the olefin. The hydrogenation product was not detected. Instead a byproduct was formed, probably via oxidative addition of nickel(0) to an allylic C-F bond to form a nickel-allyl species, which then formed a new C-H bond via C-H reductive elimination with a hydride.

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.38-7.31 (m, 4H), 7.31-7.26 (m, 1H), 4.12 (q, $J = 7.1$ Hz, 2H), 3.39 (s, 2H), 1.20 (t, $J = 7.1$ Hz, 3H).

$^{19}$F NMR (282 MHz, CDCl$_3$): $\delta$ -87.9 (dt, $J = 35.1$, 2.2 Hz), -89.2 (d, $J = 35.2$ Hz).

GC-MS (EI): Calcd for C$_{12}$H$_{12}$F$_2$O$_2$: 226.2. Found: 226.0.
IV. Deuterium labelling experiments

A general procedure using deuterated formic acid: In an argon-filled glove box, NiBr₂(DME) (2.4 mg, 0.008 mmol), (R)-Me-DuPhos (3.2 mg, 0.0096 mmol) and dry PhCF₃ (0.6 mL) were charged into a 10-mL reaction tube. Isopropanol was not used to avoid complication of H/D exchange with the solvent. After stirring for 10 min, Et₃N (56 µL, 0.4 mmol, 2 equiv), deuterio-formic acid (38 µL, 1.0 mmol, 5 equiv) and (E)-ethyl 3-phenylbut-2-enoate (0.2 mmol) were added. The reaction mixture was heated with stirring in an oil bath maintained at 80 °C for 24 h. After cooling down, the reaction mixture was diluted with 3 mL of EA/hexanes (1:4) and passed through a short plug of silica gel washing with another 5 mL of EA/hexanes (1:4). The solvent was evaporated to give the product. The deuterium content of the product was analyzed by qualitative ¹H NMR spectroscopy. The enantioselectivity (ee) of the product was determined by chiral HPLC analysis using Daicel Chiralcel OD-H, n-hexane/isopropanol 98/2, flow rate = 0.5 mL/min.

(a) \[\text{NiBr}_2(\text{DME}) 4 \text{ mol}\% \quad \text{(R)-Me-DuPhos 4.8 mol}\% \quad \text{HCO}_2\text{D} / \text{Et}_3\text{N (5.2)} \quad \text{PhCF}_3, 80 ^\circ\text{C}, 24 \text{ h} \quad 98\%, 93\% \text{ ee} \]

(b) \[\text{NiBr}_2(\text{DME}) 4 \text{ mol}\% \quad \text{(R)-Me-DuPhos 4.8 mol}\% \quad \text{HCO}_2\text{D} / \text{Et}_3\text{N (2.2)} \quad \text{PhCF}_3, 80 ^\circ\text{C}, 76 \text{ h} \quad 85\%, 93\% \text{ ee} \]

(c) \[\text{NiBr}_2(\text{DME}) 4 \text{ mol}\% \quad \text{(R)-Me-DuPhos 4.8 mol}\% \quad \text{DCO}_2\text{D} / \text{Et}_3\text{N (5.2)} \quad \text{PhCF}_3, 80 ^\circ\text{C}, 24 \text{ h} \quad 98\%, 93\% \text{ ee} \]

(d) \[\text{NiBr}_2(\text{DME}) 4 \text{ mol}\% \quad \text{(R)-Me-DuPhos 4.8 mol}\% \quad \text{HCO}_2\text{D} / \text{Et}_3\text{N (5.2)} \quad \text{PhCF}_3, 80 ^\circ\text{C}, 24 \text{ h} \]
\[
\text{Me} \quad \text{Ph} \quad \text{CO}_2\text{Et} \quad \xrightarrow{\text{NiBr}_2(\text{DME}) \ 4 \text{ mol}\% \quad (\text{R})\text{-Me-DuPhos} \ 4.8 \text{ mol}\%} \quad \text{HCO}_2\text{D} / \text{Et}_3\text{N (5:2)} \quad \text{PhCF}_3, \ 80 ^\circ \text{C}, \ 10 \text{ h} \quad 29\% \text{ D} \\
\text{Me} \quad \text{Ph} \quad \text{CO}_2\text{Et} \quad \xrightarrow{\text{D}} \quad 29\% \text{ D} \quad \text{34}\% \text{ D} \quad 60\% \text{ D} \quad 48\%, 93\% \text{ ee} \quad \text{recovered} \ 52\% \text{ yield} \\
\text{Me} \quad \text{Ph} \quad \text{CO}_2\text{Et} \quad 0\% \text{ D}