Supporting Information
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Homo-diphenylprolinol Methyl Ether as a Highly Efficient Catalyst for Asymmetric Michael Addition of Ketones to Nitroalkenes

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Supporting Information

General methods

All solvents were purified by standard procedures and distilled prior to use. Reagents obtained from commercial source were used without further purification. Petroleum ether and ethyl acetate for flash column chromatography were distilled before use. All reactions were monitored by TLC with silica gel coated plates. Flash column chromatography was performed on silica gel H (10-40 μ). NMR spectra were recorded on 300 MHz instruments. Chemical shifts (δ) are given in ppm relative to TMS, coupling constants (J) in Hz. IR spectra were recorded on a Perkin Elmer -GX spectrometer. Melting points were determined on an X-6 digital melting-point apparatus and were uncorrected. Optical rotations were measured on a Perkin Elmer 341 Polarimeter at λ = 589 nm. Analytical high performance liquid chromatography (HPLC) was carried out on WATERS 510 instrument (2487 Dual λ Absorbance Detector and 515 HPLC Pump) using chiral column. ESI HRMS was recorded on a Bruker Apex-2.

Synthesis of catalysts 3a-3r [1]

Compound 7: SOCl₂ (4 mL, 54.7 mmol) was added dropwise to a stirred and cooled (0 °C) solution of N-Cbz-homo-L-proline (12 g, 45.7 mmol) in MeOH (80 mL). After 30 min, the cold bath was removed and stirring was continued for 6 h. Evaporation of the solvent gave ester 7 as a white solid (12.56 g, ~100%), which was used for next step without further purification.

Compound 8: To a solution of 7 (22.1 g, 80 mmol) in 500 mL dry THF at -78 °C under a nitrogen atmosphere, RMgBr (240 mL 1 M solution in THF) was added dropwise. The mixture was stirred overnight and the mixture was warmed to rt. The reaction was quenched by saturated aqueous NH₄Cl, and THF was removed under
reduced pressure to give a milky residue. The residue was partitioned between ethyl acetate and 1N HCl. The organic layers were collected, washed with brine, dried over MgSO₄, filtered and concentrated to give a white solid. The crude white solid was recrystallized from Hexane/EtOAc to give pure 8 in good yields (70% ~ 94%).

**Compound 3a-3h:**
The resulting 8 were dissolved in CH₃OH (6 mL) and Pd/C (20% in weight) was added. The mixture was stirred at room temperature under a H₂ atmosphere (P=1 atm) overnight. Then, the mixture was filtered through celite and the solvent evaporated under reduced pressure to afford the crude products, which were further purified by flash column chromatography on silica gel (CH₂Cl₂ : MeOH 90 : 10) to afford the title compounds 3a-3e, 3g as white solid and 3f, 3h as light yellow oil.

![Structure of 3a](image)

**3a:** White solid, M.p. = 136 -137 °C, [α]D²⁰ = + 24.2° (c = 1.0, CHCl₃).

**1H NMR (CDCl₃, 300 MHz):** δ = 1.41 - 1.58 (m, 2H), 1.78 - 1.88 (m, 2H), 1.99 - 2.08 (dd, J = 13.9 Hz, 11.9 Hz, 1H), 2.17 (s, 1H), 2.38 - 2.44 (dd, J = 14.1 Hz, 2.98 Hz, 1H), 2.80 - 2.96 (m, 2H), 3.23 - 3.30 (m, 1H), 7.13 - 7.34 (m, 6H), 7.42 - 7.45 (d, J = 7.63 Hz, 2H), 7.52 - 7.55 (d, J = 7.59 Hz, 2H) ppm;

**13C NMR (CDCl₃, 75.5 MHz):** δ = 25.9, 32.8, 43.8, 45.5, 55.7, 78.0, 125.4, 126.0, 126.3, 127.9, 147.7, 148.8 ppm;

**IR (KBr) ν 3414, 3329, 3242, 3022, 2959, 2853, 1617, 1492, 1445, 1125, 1061, 748, 697 cm⁻¹.**

**TOF HRMS:** calcd. for C₁₈H₂₁NO [M + H]⁺ 268.1701; found 268.1703.

![Structure of 3b](image)

**3b:** White solid, M.p. = 88 - 89 °C, [α]D²⁵ = +22.3° (c = 1.0, CHCl₃).

**1H NMR (CDCl₃, 300 MHz):** δ = 1.39 - 1.55 (m, 2H), 1.76 - 1.86 (m, 2H), 1.96 - 2.05 (dd, J = 14.0 Hz, 11.9 Hz, 1H), 2.26 (s, 3H), 2.31 (s, 3H), 2.34 - 2.39 (dd, J = 14.1 Hz, 2.99 Hz, 1H), 2.81 - 2.93 (m, 2H), 3.22 - 3.29 (m, 1H), 7.05 (d, J = 8.01 Hz, 2H), 7.11 (d, J = 7.96 Hz, 2H), 7.30 (d, J = 8.15 Hz, 2H), 7.40 (d, J = 8.1 Hz, 2H) ppm;

**13C NMR (CDCl₃, 75.5 MHz):** δ = 20.89, 20.93, 25.9, 32.8, 43.9, 45.5, 55.8, 77.8, 125.3, 126.2, 128.62, 128.65, 135.4, 135.7, 144.8, 146.2 ppm; IR (KBr) ν 3412, 3329, 3242, 3022, 2959, 2853, 1613, 1508, 1409, 1180, 1086, 822, 806, 778, 729, 585, 566 cm⁻¹.

**TOF HRMS:** calcd. for C₂₀H₂₆NO [M + H]⁺ 296.2014; found 296.2083.
White solid, M.p. = 156-157 °C, $[\alpha]_{D}^{25} = +17.4^\circ$ (c = 0.5, CHCl₃).

$^1$H NMR (CDCl₃, 300 MHz): $\delta$ = 1.41 - 1.54 (m, 2H), 1.77 - 1.87 (m, 2H), 1.92 - 2.01 (dd, $J$ = 13.9 Hz, 12.0 Hz, 1H), 2.25 (s, 6H), 2.29 (s, 6H), 2.34 - 2.40 (dd, $J$ = 14.0 Hz, 2.96 Hz, 1H), 2.78 - 2.94 (m, 2H), 3.22 - 3.29 (m, 1H), 6.79 (s, 1H), 6.81 (s, 1H), 7.05 (s, 2H), 7.13 (s, 2H) ppm; $^{13}$C NMR (CDCl₃, 75.5 MHz): $\delta$ = 21.4, 21.5, 25.9, 32.8, 43.9, 45.4, 55.7, 77.8, 123.1, 124.0, 127.6, 127.9, 137.1, 137.2, 147.7, 148.9 ppm; IR (KBr) $\nu$ 3314, 2962, 2915, 2875, 1595, 1458, 1377, 1290, 1195, 1117, 897, 856, 746, 716 cm⁻¹. TOF HRMS: calcd. for C₂₂H₃₀NO [M + H]$^+$ 324.2327; found 324.2319.

White solid, M.p. = 125-126 °C, $[\alpha]_{D}^{25} = -0.048^\circ$ (c = 0.5, CHCl₃).

$^1$H NMR (CDCl₃, 300 MHz): $\delta$ = 1.50 - 1.64 (m, 2H), 1.85 - 1.96 (m, 2H), 1.98 - 2.07 (dd, $J$ = 14.1 Hz, 12.2 Hz, 1H), 2.45 - 2.50 (dd, $J$ = 14.3 Hz, 2.97 Hz, 1H), 2.81 - 2.90 (m, 1H), 2.98 - 3.05 (m, 1H), 3.24 - 3.32 (m, 1H), 7.73 (s, 1H), 7.78 (s, 1H), 7.90 (s, 2H), 8.03 (s, 2H) ppm; $^{13}$C NMR (CDCl₃, 75.5 MHz): $\delta$ = 25.9, 32.7, 43.1, 45.4, 55.5, 77.4, 117.8, 121.1 (q), 121.5, 125.1, 125.4, 125.5, 126.3, 128.7, 131.4 (q), 132.2, 132.4, 132.3 (q), 149.3, 150.0 ppm; IR (KBr) $\nu$ 3339, 3087, 2968, 1622, 1462, 1374, 1278, 1122, 1027, 982, 890, 842, 710, 681 cm⁻¹. TOF HRMS: calcd. for C₂₂H₁₈F₁₂NO [M + H]$^+$ 540.1197; found 540.1223.

White solid, M.p. = 137-138 °C, $[\alpha]_{D}^{25} = +92.2^\circ$ (c = 0.5, CHCl₃).

$^1$H NMR (CDCl₃, 300 MHz): $\delta$ = 1.43 - 1.56 (m, 2H), 1.77 - 1.88 (m, 2H), 2.19 - 2.28 (dd, $J$ = 13.9 Hz, 12.0 Hz, 1H), 2.60 - 2.65 (dd, $J$ = 14.0 Hz, 2.96 Hz, 1H), 2.82 - 2.95 (m, 2H), 3.25 - 3.31 (m, 1H), 7.36 - 7.49 (m, 5H), 7.56 - 7.59 (dd, $J$ = 8.6 Hz, 1.64 Hz,
1H), 7.69 - 7.81 (m, 5H), 7.88 (d, J = 7.5 Hz, 1H), 7.93 (s, 1H), 8.24 (s, 1H) ppm; 13C NMR (CDCl3, 75.5 MHz): δ = 26.0, 32.8, 43.2, 45.5, 55.7, 78.4, 123.2, 124.6, 125.0, 125.2, 125.5, 125.57, 125.7, 125.9, 127.3, 127.4, 127.6, 127.8, 128.1, 128.2, 132.0, 132.2, 133.0, 133.2, 145.1, 145.7 ppm; IR (KBr) ν 3416, 3326, 3056, 2956, 2866, 1626, 1597, 1503, 1418, 1355, 1110, 860, 817, 785, 745, 478 cm⁻¹. TOF HRMS: calcd. for C26H26NO [M + H]⁺ 368.2014; found 368.1974.

\[\text{Colorless oil, } [\alpha]_D^{25} = +14.4^\circ (c = 1.0, \text{ CHCl}_3). \]

1H NMR (CDCl3, 300 MHz): δ = 0.89 - 0.98 (m, 6H), 1.42 - 1.68 (m, 6H), 1.81 - 1.87 (m, 2H), 1.99 - 2.08 (dd, J = 13.7 Hz, 12.1 Hz, 1H), 2.37 - 2.42 (dd, J = 14.1 Hz, 2.78 Hz, 1H), 2.49 - 2.59 (m, 4H), 2.83 - 2.93 (m, 2H), 3.26 - 3.29 (m, 1H), 7.06 - 7.14 (m, 4H), 7.35 (d, J = 8.07 Hz, 2H), 7.44 (d, J = 8.0 Hz, 2H) ppm; 13C NMR (CDCl3, 75.5 MHz): δ = 13.8, 13.9, 24.45, 24.47, 25.9, 32.7, 37.56, 37.59, 44.0, 45.4, 55.8, 77.8, 125.2, 126.1, 127.9, 128.0, 140.1, 140.5, 144.9, 146.4 ppm; IR (neat) ν 2958, 1613, 1452, 1295, 1260, 1182, 1101, 1018, 841, 745, 602 cm⁻¹. TOF HRMS: calcd. for C24H34NO [M + H]⁺ 352.264; found 352.264.

\[\text{White solid, M.p.} = 76-77^\circ C, [\alpha]_D^{25} = +22.3^\circ (c = 1.0, \text{ CHCl}_3). \]

1H NMR (CDCl3, 300 MHz): δ = 0.83 - 0.90 (q, J = 14.3 Hz, 6H), 1.27 - 1.45 (m, 9H), 1.47 - 1.61 (m, 5H), 1.78 - 1.82 (m, 2H), 1.94 - 2.03 (dd, J = 13.7 Hz, 12.1 Hz, 1H), 2.33 - 2.39 (dd, J = 14.0 Hz, 2.7 Hz, 1H), 2.49 - 2.58 (m, 4H), 2.81 - 2.90 (m, 2H), 3.26 (m, 1H), 7.06 (d, J = 8.1 Hz, 2H), 7.11 (d, J = 8.0 Hz, 2H), 7.32 (d, J = 8.1 Hz, 2H), 7.42 (d, J = 8.0 Hz, 2H) ppm; 13C NMR (CDCl3, 75.5 MHz): δ = 13.9, 14.0, 22.50, 22.52, 26.0, 31.0, 31.1, 31.4, 31.6, 32.8, 35.40, 35.47, 44.0, 45.4, 55.7, 77.8, 125.2, 126.1, 127.8, 127.9, 140.4, 140.7, 145.0, 146.4 ppm; IR (KBr) ν 3329, 3271, 3026, 2998, 2926, 2854, 1615, 1573, 1508, 1461, 1412, 1377, 1290, 1128, 1105, 904,
Yellowish oil, \([\alpha]_D^{25} = -1.1^\circ\) (c = 0.5, CHCl₃). \(^1\)H NMR (CDCl₃, 300 MHz): \(\delta = 0.80 - 0.87\) (m, 6H), 1.40 - 1.53 (m, 5H), 1.55 - 2.03 (m, 5H), 3.09 - 3.13 (m, 1H), 3.27 - 3.36 (m, 1H), 3.53 - 4.02 (m, 1H), 5.87 (s, 2H) ppm; \(^{13}\)C NMR (CDCl₃, 75.5 MHz): \(\delta = 7.36, 8.38, 23.9, 28.3, 31.8, 32.4, 40.7, 45.0, 55.4, 73.8\) ppm; IR (neat) \(\nu = 3283, 2964, 1617, 1533, 1412, 1283, 1148, 1041, 978, 811, 626\) cm\(^{-1}\). TOF HRMS: calcd. for C₁₀H₂₂NO [M + H]\(^+\) 172.1701; found 172.1678.

Compound 3i and 3j: To a solution of homo-diphenylprolinol 8a (481 mg, 1.2 mmol) in CH₂Cl₂ (1.2 mL) was added 2,6-lutidine (1.2 mL, 8.3 mmol) and TESOTf (1.3 mL, 5.9 mmol) or TBSOTf (2 mL, 5.9 mmol) at 0 °C. The reaction mixture was stirred for 24 h at room temperature and quenched with aq. NH₄Cl and the organic materials were extracted with ethyl acetate. The organic layers were dried over anhydrous Na₂SO₄, and concentrated in vacuo after filtration. To the residue, MeOH and aq. NaHCO₃ were added, and the mixture was stirred at room temperature. Extracted with ethyl acetate and the organic phase was dried over with anhydrous Na₂SO₄ and concentrated in vacuo after filtration. Purification by silica gel column chromatography (ethyl acetate: hexane = 10:1 ~ 2:1) to gave 3i in 79% yield, and 3j in 85% yield.

Yellowish oil, \([\alpha]_D^{25} = + 79.9^\circ\) (c = 1, CHCl₃). \(^1\)H NMR (CDCl₃, 300 MHz): \(\delta = 0.30 - 0.38\) (q, \(J = 15.8\) Hz, 6H), 0.85 (t, \(J = 7.89\) Hz, 9H), 1.47 - 1.54 (m, 1H), 1.73 - 1.86 (m, 2H), 1.93 - 2.0 (m, 1H), 2.64 - 2.71 (dd, \(J = 13.8\) Hz, 7.43 Hz, 1H), 2.92-2.99 (dd, \(J = 13.9\) Hz, 5.4 Hz, 1H), 3. 20-3.36 (m, 3H), 7.28-7.33 (m,10H)
ppm; $^{13}$C NMR (CDCl$_3$, 75.5 MHz): $\delta = 6.0, 7.0, 23.4, 30.6, 44.2, 44.9, 58.5, 79.9, 127.10, 127.18, 127.68, 128.1, 128.3, 145.1, 145.2$ ppm; IR (neat) $\nu =$ 3457, 3062, 2879, 2801, 1601, 1494, 1448, 1404, 1273, 1122, 1058, 1031, 779, 758, 701, 639, 518 cm$^{-1}$. TOF HRMS: calcd. for C$_{24}$H$_{36}$NOSi [M + H]$^+$ 382.2566; found 382.2630.

Yellowish oil, $[\alpha]_D^{25} = +5.0^\circ$ (c = 1, CHCl$_3$). $^1$H NMR (CDCl$_3$, 300 MHz): $\delta = -0.36$ (s, 3H), -0.29 (s, 3H), 0.96 (s, 9H), 1.13 - 1.16 (m, 1H), 1.45 - 1.58 (m, 2H), 1.65 - 1.67 (m, 1H), 2.56-2.69 (m, 4H), 2.83-2.88 (m, 1H), 3.13-3.18 (m, 1H), 7.20-7.36 (m, 10H) ppm; $^{13}$C NMR (CDCl$_3$, 75.5 MHz): $\delta = -3.16$, -2.89, 18.7, 23.8, 26.2, 31.9, 45.6, 47.3, 55.0, 79.8, 127.0, 127.1, 127.4, 127.7, 127.9, 147.3, 147.6 ppm; IR (neat) $\nu =$ 3477, 2930, 2857, 1602, 1493, 1447, 1285, 1068, 10301, 835, 777, 701, 639, 575 cm$^{-1}$. TOF HRMS: calcd. for C$_{24}$H$_{36}$NOSi [M + H]$^+$ 382.2566; found 382.2165.

**Compound 9 and 10:** 8a (24.8 g, 62 mmol) was dissolved in 2 mL MeI or EtI and 10 mL THF, NaH (310 mmol) was added slowly to the stirred mixture over a course of 30 min. at 0 °C under N$_2$. The reaction mixture was then stirred overnight and quenched with water. Excess MeI was removed under reduced pressure in a well-ventilated hood (Note: avoid MeI vapor in the laboratory). The residue was dissolved in ethyl acetate and partitioned between ethyl acetate and water. The organic layers were collected, washed with brine, dried over with MgSO$_4$, filtered and concentrated to give colorless oil. The oil was eluted through a SiO$_2$ column by EtOAc/Hexane gave pure 9 and 10 with yields 60 ~ 80%.

**Compound 3k-3q and 3r:** The resulting 9 or 10 was dissolved in CH$_3$OH (6 mL) and Pd/C (20% in weight) was added. The mixture was stirred at room temperature under
a H₂ atmosphere (P = 1 atm) overnight. Then, the mixture was filtered through celite and the solvent evaporated under reduced pressure to afford the crude product, which was further purified by flash column chromatography on silicagel (CH₂Cl₂ : MeOH = 90 : 10) to afford the title compounds 3k-3m, 3o as white solid and 3n, 3p, 3q and 3r as light yellow oil.

White solid, M.p. = 86 - 87 °C, [α]D25 = +27.0° (c = 1.0, CHCl₃). ¹H NMR (CDCl₃, 300 MHz): δ = 1.17 - 1.23 (m, 1H), 1.50 - 1.71 (m, 3H), 1.90 (s, 1H), 2.46 - 2.52 (dd, J = 14.2 Hz, 4.65 Hz, 1H), 2.56 - 2.68 (m, 2H), 2.76 - 2.82 (m, 1H), 2.87 - 2.94 (m, 1H), 3.06 (s, 3H), 7.17 - 7.36 (m, 10H) ppm; ¹³C NMR (CDCl₃, 75.5 MHz): δ = 23.8, 32.1, 40.9, 45.7, 50.5, 54.5, 82.3, 126.5, 126.7, 126.8, 127.0, 127.8, 127.9, 145.3, 145.5 ppm; IR (KBr) ν 3416, 3363, 3022, 2958, 2826, 1618, 1599, 1491, 1444, 1400, 1189, 1155, 1122, 1065, 916, 849, 752, 698, 621, 594 cm⁻¹. TOF HRMS: calcd. for C₁₉H₂₄NO [M + H]⁺ 282.1858; found 282.1832.

White solid, M.p. = 55 - 56 °C, [α]D25 = +17.0° (c = 1.0, CHCl₃). ¹H NMR (CDCl₃, 300MHz): δ = 1.25 - 1.28 (m, 2H), 1.58 - 1.63 (m, 2H), 1.77 (m, 1H), 2.29 (s, 6H), 2.48 - 2.54 (dd, J = 14.1 Hz, 5.6 Hz, 1H), 2.75 - 2.85 (m, 2H), 2.95 - 3.00 (m, 1H), 3.06 (s, 3H), 5.15 (s, 1H), 7.07 (d, J = 7.93 Hz, 4H), 7.19 - 7.24 (m, 4H) ppm; ¹³CNMR (CDCl₃, 75.5 MHz): δ = 20.92, 20.94, 23.6, 31.5, 40.1, 44.9, 50.7, 55.4, 82.0, 126.7, 127.0, 128.6, 128.70, 128.79, 136.1, 136.4, 141.5, 142.0 ppm; IR (KBr) ν 3414, 3367, 3020, 2959, 2866, 2818, 1614, 1509, 1456, 1402, 1288, 1266, 1183, 1085, 1064, 809, 779, 731, 672, 576 cm⁻¹. TOF HRMS: calcd. for C₂₁H₂₈NO [M + H]⁺ 310.2171; found 310.2173.

Colorless oil, [α]D25 = +20.2° (c = 1.0, CHCl₃). ¹H NMR (CDCl₃, 300 MHz): δ = 1.18 - 1.25 (m, 1H), 1.53 - 1.69 (m, 3H), 2.26 (s, 12H), 2.40 - 2.46 (dd,
$J = 14.3$ Hz, 4.7 Hz, 1H), 2.49 - 2.56 (dd, $J = 14.2$ Hz, 6.4 Hz, 1H), 2.62 - 2.65 (m, 1H), 2.76 - 2.80 (m, 1H), 2.87 - 2.93 (m, 1H), 3.04 (s, 3H), 6.82 (s, 2H), 6.93 (s, 2H), 6.95 (s, 2H) ppm; $^{13}$C NMR (CDCl$_3$, 75.5 MHz): $\delta = 21.45, 21.49, 23.81, 23.87, 32.0, 40.8, 45.6, 50.4, 54.5, 82.2, 124.5, 124.7, 128.0, 128.3, 137.0, 137.1, 145.2, 145.5 ppm; IR (neat) $\nu = 3349, 2940, 2867, 2827, 1740, 1601, 1458, 1400, 1289, 1241, 1159, 1094, 1038, 851, 748, 724, 655$ cm$^{-1}$. TOF HRMS: calcd. for C$_{23}$H$_{32}$NO [M + H]$^+$ 338.2484; found 338.2452.

.colorless oil, $[\alpha]_D^{25} = + 40.6^\circ$ (c = 1.0, CHCl$_3$). $^1$H NMR (CDCl$_3$, 300 MHz): $\delta = 1.05 - 1.14$ (m, 1H), 1.51 - 1.83 (m, 4H), 2.50 - 2.57 (m, 1H), 2.68 - 2.79 (m, 3H), 2.91 - 2.98 (m, 1H), 3.15 (s, 3H), 7.79 - 7.81 (m, 6H) ppm; $^{13}$C NMR (CDCl$_3$, 75.5 MHz): $\delta = 24.5, 32.3, 40.9, 45.9, 51.0, 53.9, 81.4, 121.3$ (d), 121.6 (m), 121.9 (m), 124.9 (d), 126.6 (m), 127.0 (m), 131.7 (q), 132.3 (q), 146.6, 147.1 ppm; IR (neat) $\nu = 3361, 3100, 2947, 2877, 2837, 1712, 1624, 1465, 1378, 1291, 1121, 1002, 900, 844, 805, 709, 683, 581$ cm$^{-1}$. TOF HRMS: calcd. for C$_{23}$H$_{20}$F$_{12}$NO [M + H]$^+$ 554.1353; found 554.1309.

.white solid, M.p. = 68 - 72°C, $[\alpha]_D^{25} = -25.5$ (c = 0.5, CHCl$_3$). $^1$H NMR (CDCl$_3$, 300 MHz): $\delta = 1.20 - 1.35$ (m, 4H), 1.53 - 1.63 (m, 2H), 1.77 - 1.79 (m, 1H), 2.84 - 3.02 (m, 2H), 3.15 (s, 3H), 3.25 (d, $J = 11.4$ Hz, 1H), 7.19 - 7.28 (m, 2H), 7.44 (br, 4H), 7.62 - 7.85 (m, 6H), 8.04 (s, 1H), 8.11 (s, 1H) ppm; $^{13}$C NMR (CDCl$_3$, 75.5 MHz): $\delta = 23.6, 29.6, 31.1, 37.7, 43.8, 50.8, 55.9, 81.9, 125.0, 125.3, 125.7, 126.0, 126.1, 127.41, 127.43, 127.7, 128.1, 128.2, 128.3, 132.2, 132.4, 132.8, 132.9, 141.0, 141.7 ppm; IR (KBr) $\nu = 3422, 3359, 3053, 3019, 2962, 2909, 2877, 2834, 1629, 1598, 1504, 1433, 1396, 1123, 1076, 1061, 895, 858, 821, 786, 740, 655$ cm$^{-1}$. TOF HRMS: calcd. for C$_{27}$H$_{28}$NO [M + H]$^+$ 382.2171; found 382.2630.
Colorless oil, \([\alpha]_D^{25} = +14.0^\circ\) (c = 1.0, CHCl\(_3\)). \(^1\)H NMR (CDCl\(_3\), 300 MHz): \(\delta = 0.90\) (t, \(J = 7.3\) Hz, 6H), 1.16 - 1.23 (m, 2H), 1.48 - 1.70 (m, 7H), 2.43 - 2.64 (m, 7H), 2.79 - 2.92 (m, 2H), 3.04 (s, 3H), 7.05 - 7.08 (m, 4H), 7.22 - 7.27 (m, 4H) ppm; \(^{13}\)C NMR (CDCl\(_3\), 75.5 MHz): \(\delta = 13.6, 13.7, 23.6, 24.1, 24.2, 31.8, 37.4, 40.9, 45.4, 50.3, 54.4, 81.9, 126.5, 126.7, 127.7, 127.8, 140.5, 140.7, 142.4, 142.6\) ppm; IR (neat) \(\nu = 3356, 3022, 2958, 2869, 1614, 1509, 1459, 1409, 1183, 1096, 1020, 867, 840, 746, 589\) cm\(^{-1}\). TOF HRMS: calcd. for C\(_{25}\)H\(_{36}\)NO [M + H]\(^+\) 366.2797; found 366.2790.

Colorless oil, \([\alpha]_D^{25} = +17.5^\circ\) (c = 1.0, CHCl\(_3\)). \(^1\)H NMR (CDCl\(_3\), 300 MHz): \(\delta = 0.85 - 0.89\) (t, \(J = 6.0\) Hz, 6H), 1.25 - 1.42 (m, 10H), 1.55 - 1.58 (m, 5H), 1.69 - 1.78 (m, 1H), 1.92 - 1.94 (m, 1H), 2.50 - 2.62 (m, 5H), 3.06 (s, 3H), 3.20 - 3.25 (m, 2H), 3.31 - 3.40 (m, 2H), 7.05 - 7.10 (m, 4H), 7.22 - 7.39 (m, 4H) ppm; \(^{13}\)C NMR (CDCl\(_3\), 75.5 MHz): \(\delta = 13.9, 14.04, 22.4, 22.5, 23.1, 29.6, 30.7, 30.96, 31.4, 31.54, 35.42, 35.45, 39.1, 43.8, 51.3, 57.1, 82.0, 125.9, 126.1, 126.7, 127.5, 128.1, 129.5, 139.9, 140.8, 141.1, 142.1 pm); IR (neat) \(\nu = 3359, 3022, 2928, 2856, 1614, 1510, 1462, 1410, 1183, 1099, 1076, 1020, 838, 728, 682, 587\) cm\(^{-1}\). TOF HRMS: calcd. for C\(_{29}\)H\(_{44}\)NO [M + H]\(^+\) 422.3423; found 422.3394.

Colorless oil, \([\alpha]_D^{25} = +9.1^\circ\) (c = 0.5, CHCl\(_3\)). \(^1\)H NMR (CDCl\(_3\), 300 MHz): \(\delta = 1.17\) (t, \(J = 6.9\) Hz, 3H), 1.48 - 1.71 (m, 3H), 2.47 - 2.53 (dd, \(J = 14.1\) Hz, 4.8 Hz, 1H), 2.61 - 2.67 (m, 3H), 2.81 - 2.86 (m, 1H), 2.88 - 2.92 (m, 1H), 3.10 - 3.15 (m, 1H), 3.22 - 3.27 (m, 1H), 7.10 - 7.38 (m, 10H) ppm; \(^{13}\)C NMR (CDCl\(_3\), 75.5
MHz): $\delta = 15.3, 23.7, 31.9, 41.2, 45.5, 54.6, 57.6, 81.6, 126.4, 126.61, 126.68, 126.8, 127.7, 127.8, 145.7, 145.9$ ppm; IR (neat) $\nu = 3352, 3058, 3025, 2970, 2874, 1599, 1491, 1446, 1398, 1260, 1191, 1158, 1113, 1070, 955, 845, 812, 778, 752, 700, 626, 559$ cm$^{-1}$. TOF HRMS: calcd. for C$_{20}$H$_{26}$NO $[M + H]^+$ 296.2014; found 296.2031.

Asymmetric Michael addition of ketones to nitroolefins

![Chemical structure diagram]

**General procedure:** To a stirred solution of catalyst (0.05 equiv) in hexane (0.5 mL) and ketone (3 equiv.) at room temperature, was added o-Methylbenzoic acid (0.05 equiv) and, after 5 minutes, nitroolefin (1 equiv.) was added. The reaction mixture was stirred at room temperature for the appropriate time. The solvent was evaporated and the residue was chromatography on SiO$_2$-column (hexane/ethyl acetate = 10:1) to afford the desired product. The enantiomeric excess of the product was determined by chiral HPLC analysis (Daicel Chiralpak AS-H or AD-H). Relative and absolute configuration of the products was determined by comparison with literature data.$^{[2 - 4]}$. The enantiomeric excess of new products was determined according to compare with their corresponding racemic peaks.

White solid, M.p. = 95 – 96 °C, $[\alpha]_D^{25} = -34.1 ^\circ$ (c = 1, CHCl$_3$). $^1$H NMR (CDCl$_3$, 300 MHz): $\delta = 1.19 - 1.24$ (m, 1H), 1.50 - 1.75 (m, 4H), 2.05 - 2.10 (m, 1H), 2.35 (s, 3H), 2.38 - 2.43 (m, 1H), 2.62 - 2.67 (m, 1H), 4.08 - 4.16 (m, 1H), 4.56 - 4.63 (dd, $J = 12.3$ Hz, 10.3 Hz, 1H), 4.97 - 5.02 (dd, $J = 12.6$ Hz, 4.3 Hz, 1H), 7.09 - 7.21 (m, 4H); $^{13}$C NMR (CDCl$_3$, 75.5 MHz): $\delta = 19.8, 25.2, 28.6, 32.7, 38.1, 42.7, 53.2, 78.6, 125.5, 126.5, 127.1, 130.8, 136.3, 137.2, 212.2$; The enantiomeric excess was determined by HPLC with a AD-H column at 2 54 nm. (2-propanol : hexane=10:90), 0.5 mL/min; $t_s = 16.7$ min (minor), 22.5 min (major).

**References:**


NMR spectra for new catalysts and part of the Michael addition products
Part of the HPLC Analysis Data

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