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Supporting Information

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Pd-Catalysed Cleavage of Benzylic-Nitro Bonds: New Opportunities for Asymmetric Synthesis**

Thomas C. Fessard, Hajime Motoyoshi and Erick M. Carreira*

*Prof. Dr. Erick M. Carreira
Laboratorium für Organische Chemie
ETH Hönggerberg, HCI H335
8093 Zürich, Switzerland
Fax: (++41)-1-632-1328
E-mail: carreira@org.chem.ethz.ch

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The solvents used for the reactions were purified by distillation and dried by passage over activated alumina under an argon atmosphere. DMF was not distilled but dried over molecular sieves (4Å). Methanol, ethanol and *iso*-propanol were of analytical grade and used as received. For flash chromatography and extractions, technical grade solvents were used, which were distilled prior to use. All chemicals were purchased from ACROS, Aldrich, Fluka or Lancaster and used as received unless noted otherwise.

Hydrogenation reactions were performed under atmospheric pressure using rubber balloons filled with hydrogen connected to the reaction flask. Hydrogen was obtained from a BocGas cylinder. Deuterium 99.8%D was obtained from Aldrich in a 25 L cylinder. CD_3OD 99.8%D was purchased from ARMAR Chemicals.

Chromatographic purification was performed as flash chromatography using Merck silica gel 160. TLC analyses where performed on Merck silica gel 160 F_{254} TLC glass or aluminium plates and visualized with UV light and/or ceric ammonium molybdate (CAM) stain.

^{1}H-NMR spectra were recorded on a VARIAN Mercury 300 MHz spectrometer in chloroform-*d*. All signals are reported in ppm relative to TMS. The data is reported as (s=singlet, d=doublet, t= triplet, q=quartet, m=multiplet, br=broad, coupling constant(s) in Hz, integration). ^{13}C-NMR spectra were recorded with ^{1}H-decoupling on VARIAN Mercury 75 MHz in chloroform-*d*, all signals are reported in ppm relative to TMS.

Infrared spectra were recorded on a Perkin-Elmer spectrum RX-I FT-IR spectrometer as thin films, KBr disk or solution in $CHCl_3$. The data is being reported as absorption maxima (ν, cm^{-1}).

Melting points were measured on Büchi 510 melting point apparatus using open glass capillaries and are uncorrected.

Mass spectrometry measurements were performed by the mass spectrometry service of the LOC at the ETHZ.

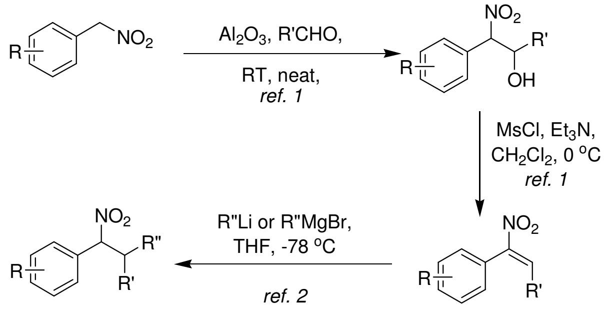
Combustion analyses were performed by the Mikroelementar-analytisches Laboratorium of the LOC at the ETHZ.

Enantiomeric excesses were determined by chiral HPLC analysis with Merck-Hitachi D-7000 system. Columns used, solvent mixtures and conditions are given in parentheses, followed by retention times and enantiomeric excesses measured.

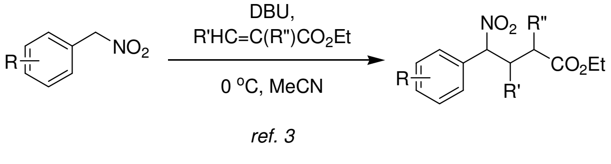
Optical rotation $[\alpha]_D$ were measured with a Jasco DID-1000 Polarimeter, 10 cm, 1 mL cell. Concentrations (c, g/100 mL) and solvents are given in parentheses.

The substrates **1, 6, 8, 10, 14, 16, 18, 20** (Scheme A)[1,2] and **22, 24, 26, 28** (Scheme B)[3] were prepared using known methods.

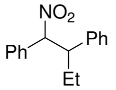
Scheme A.



Scheme B.



1,2-diphenyl-nitrobutane (1)



Prepared according to conditions given in Scheme A;

White solid; mp. 86-87 °C; mixture of two diastereoisomers;

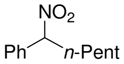
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68-6.96 (m, 10 H), 5.64 (d, 1 H minor, *J* = 11.5 Hz), 5.62 (d, 1 H major, *J* = 11.3 Hz), 3.68-3.51 (m, 1 H), 1.89-1.72 (m, 2 H major), 1.45-1.33 (m, 2 H minor), 0.79 (s, 3 H major, *J* = 7.1 Hz), 0.65 (s, 3 H minor, *J* = 7.1 Hz);

^{13}C NMR (75 MHz, $CDCl_3$) δ 138.9, 133.5, 133.2, 130.0, 129.3, 129.0, 128.6, 128.4, 128.1, 127.9, 127.5, 126.9, 96.8, 96.5, 51.4, 51.2, 26.1, 24.9, 11.4;

FTIR (thin film, cm^{-1}) ν 3018, 2964, 2919, 2865, 1548, 1495, 1455, 1361, 719, 697;

EA calcd for $C_{15}H_{15}NO_2$ C 74.67, H 6.27, N 5.80. Found C 74.61, H 6.31, N 5.78.

(1-nitrohexyl)benzene (4)[4]

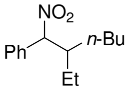


Colourless oil;

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55-7.35 (m, 5 H), 5.45 (dd, 1 H, *J* = 8.7, 6.5 Hz), 2.58-2.40 (m, 1 H), 2.15-1.97 (m, 1 H), 1.45-1.20 (m, 6 H), 0.88 (t, 3 H, *J* = 6.5 Hz);

^{13}C NMR (75 MHz, $CDCl_3$) δ 134.9, 129.9, 129.2, 127.9, 91.8, 30.1, 31.3, 25.9, 22.5, 14.1.

(2-ethyl-1-nitrohexyl)benzene (6)



Prepared following conditions given in Scheme A;

Colourless oil; mixture of two diastereoisomers;

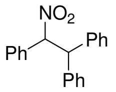
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55–7.47 (m, 2 H), 7.45–7.38 (m, 3 H), 5.32 (d, 1 H major, *J* = 11.2 Hz), 5.31 (d, 1 H minor, *J* = 11.2 Hz), 2.63–2.49 (m, 1 H), 1.62–1.02 (m, 3H), 0.96 (t, 3 H major, *J* = 7.5 Hz), 0.74 (t, 3 H minor, *J* = 7.8 Hz);

^{13}C NMR (75 MHz, $CDCl_3$) δ 133.8, 129.7, 128.9, 128.3, 95.8, 95.5, 42.0, 28.5, 27.8, 27.5, 27.0, 23.0, 22.8, 21.9, 20.7, 14.1, 13.9, 9.5, 9.3;

FTIR (thin film, cm^{-1}) ν 2962, 2934, 2873, 1552, 1498, 1456, 1360, 1296, 1269, 722, 695;

EA calcd for $C_{14}H_{21}NO_2$ C 71.46, H 8.99, N 5.95. Found C 71.20, H 9.01, N 6.01.

1,1,2-triphenyl-nitroethane (8)



Prepared from *trans*-nitrostilbene[5] and phenyllithium according to Scheme A;

White solid; mp. 102–104 °C;

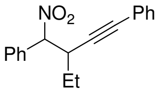
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54–7.44 (m, 4 H), 7.39–7.22 (m, 6 H), 7.16–7.04 (m, 5 H), 6.31 (d, 1 H, *J* = 12.1 Hz), 5.11 (d, 1 H, *J* = 12.1 Hz);

^{13}C NMR (75 MHz, $CDCl_3$) δ 140.0, 138.8, 133.2, 130.0, 129.2, 129.0, 128.9, 128.5, 128.5, 127.8, 127.6, 127.2, 95.9, 55.3;

FTIR (thin film, cm^{-1}) ν 3064, 3032, 2927, 1601, 1548, 1496, 1253, 1360, 1274, 1076, 746, 719, 694;

EA calcd for $C_{20}H_{17}NO_2$ C 79.19, H 5.65, N 4.62. Found C 79.07, H 5.84, N 4.71.

1-phenyl-2-(phenylacetynyl)-nitrobutane (10)



Prepared following conditions given in Scheme A;

White solid; mp. 94-96 °C; mixture of two diastereoisomers;

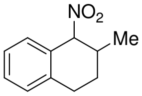
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63-7.11 (m, 10 H), 5.51 (d, 1 H major, *J* = 11.2 Hz), 5.49 (d, 1 H minor, *J* = 10.3 Hz), 3.82-3.64 (m, 1 H), 1.85-1.24 (m, 2 H), 1.21 (t, 3 H minor, *J* = 7.2 Hz), 1.08 (t, 3 H major, *J* = 7.2 Hz);

^{13}C NMR (75 MHz, CDCl3) δ 133.3, 132.2, 131.7, 131.4, 130.2, 129.9, 129.1, 128.7, 128.3, 128.2, 128.2, 128.1, 128.0, 122.6, 94.8, 93.3, 86.9, 86.1, 85.9, 84.8, 38.9, 38.4, 25.5, 23.9, 11.4, 11.3;

FTIR (thin film, cm^{-1}) ν 2968, 2927 2864, 1552, 1488, 1455, 1362, 759, 732, 693;

HRMS (EI) *m/z* calculated for $C_{18}H_{17}NO_2$ ($[M]^+$) 279.1254, found 279.1258.

2-methyl-1-nitro-1,2,3,4-tetrahydronaphthalene (12)



Prepared by treatment of 2-methyl-3,4-dihydronaphtalene with N_2O_4 and triethylamine,[6] followed by reduction with $NaBH_4$;

Colourless oil; mixture of two diastereoisomers;

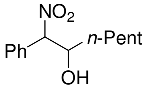
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35-7.15 (m, 4 H), 5.67 (d, 1 H minor, *J* = 4.4 Hz), 5.47 (d, 1 H major, *J* = 8.0 Hz), 3.08-2.77 (m, 3 H), 2.69-2.55 (m, 1 H), 2.30-2.00 (m, 2 H), 1.81-1.72 (m, 1 H minor), 1.66-1.51 (m, 1 H), 1.18 (d, 3 H minor, *J* = 7.4 Hz), 1.16 (d, 3 H major, *J* = 6.6 Hz);

^{13}C NMR (75 MHz, $CDCl_3$) δ 138.0, 137.3, 129.6, 129.3, 129.1, 129.0, 127.6, 127.0, 126.2, 93.2, 89.9, 34.1, 32.7, 28.5, 27.6, 27.4, 24.5, 18.4, 17.8;

FTIR (thin film, cm^{-1}) ν 2931, 1546, 1495, 1456, 1363, 1274, 790;

HRMS (EI) *m/z* calculated for $C_{11}H_{13}$ ($[M-NO_2]^+$) 145.1017, found 145.1044.

1-nitro-1-phenyl-heptan-2-ol (14)



Prepared following conditions given in Scheme A;

Colourless oil; mixture of two diastereoisomers;

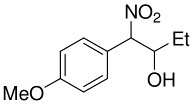
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56–7.37 (m, 5 H), 5.35 (d, 1 H, J = 12.6 Hz), 4.62–4.50 (m, 1 H), 2.59 (d, 1 H major, J = 5.2 Hz), 2.27 (d, 1 H minor, J = 4.4 Hz), 1.54–1.08 (m, 8 H), 0.83 (t, 3 H, J = 6.9 Hz);

^{13}C NMR (75 MHz, $CDCl_3$) δ 132.0, 131.3, 130.1, 130.0, 129.1, 129.0, 128.9, 128.0, 96.7, 93.9, 72.4, 72.0, 33.2, 32.1, 31.4, 24.9, 24.5, 22.4, 22.3, 15.1, 13.8;

FTIR (thin film, cm^{-1}) ν 2931, 2361, 1557, 1365, 728, 632;

EA calcd for $C_{13}H_{19}NO_3$ C 65.80, H 8.07, N 5.90. Found C 66.06, H 8.35, N 5.97.

1-(4′-methoxyphenyl)-1-nitrobutan-2-ol (16)



Prepared following conditions given in Scheme A;

Colourless oil; mixture of diastereoisomers;

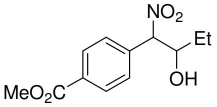
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46 (d, 2 H minor, J = 8.7 Hz), 7.28 (d, 2 H major, J = 8.7 Hz), 6.92 (d, 2 H minor, J = 8.4 Hz), 6.90 (d, 2 H major, J = 8.7 Hz), 5.32 (d, 1 H major, J = 10.0 Hz), 5.30 (d, 1 H minor, J = 6.9 Hz), 6.50–6.35 (m, 1 H), 3.79 (s, 3 H minor), 3.78 (s, 3 H major), 2.97 (d, 1 H major, J = 5.6 Hz), 2.54 (d, 1 H minor, J = 4.3 Hz), 1.58–1.15 (m, 2 H), 1.00 (t, 3 H minor, J = 7.2 Hz), 0.91 (t, 3 H major, J = 7.5 Hz);

^{13}C NMR (75 MHz, $CDCl_3$) δ 161.1, 161.0, 130.8, 129.7, 124.5, 123.7, 114.7, 114.5, 96.3, 93.5, 78.9, 73.5, 55.5, 26.7, 25.6, 9.9, 9.5;

FTIR (thin film, cm^{-1}) ν 3436, 2970, 1612, 1552, 1515, 1463, 1375, 1307, 1254, 1180, 1115, 1031, 980, 834, 794, 758;

EA calcd for $C_{11}H_{15}NO_4$ C 58.66, H 6.71, N 6.22. Found C 58.43, H 6.81, N 6.13.

methyl 4-(2-hydroxy-1-nitrobutyl)benzoate (18)



Prepared following conditions given in Scheme A;

Colourless oil; mixture of two diastereoisomers;

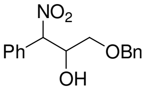
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.07 (d, 2 H, *J* = 8.1 Hz), 7.55 (d, 2 H, *J* = 8.4 Hz), 5.41 (d, 1 H, *J* = 9.6 Hz), 4.55–4.44 (m, 1 H), 3.93 (s, 3 H), 2.66 (d, 1 H, *J* = 5.6 Hz), 1.34–1.22 (m, 2 H), 0.94 (t, 3 H, *J* = 7.5 Hz);

^{13}C NMR (75 MHz, $CDCl_3$) δ 166.4, 136.6, 132.0, 130.6, 130.2, 129.6, 128.4, 96.1, 73.9, 52.6, 25.6, 9.5;

FTIR (thin film, cm^{-1}) ν 3445, 2970, 1723, 1557, 1437, 1372, 1284, 1190, 1113, 787, 742;

EA calcd for $C_{12}H_{15}NO_5$ C 56.91, H 5.97, N 5.53. Found C 56.85, H 6.01, 5.58.

3-(benzyloxy)-1-nitro-1-phenylpropan-2-ol (20)



Prepared following conditions given in Scheme A;

Colourless crystals; mp. 71–74 °C; mixture of two diastereoisomers;

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52–7.22 (m, 10 H), 5.65 (d, 1 H minor, *J* = 6.9 Hz), 5.63 (d, 1 H major, *J* = 10.2 Hz), 4.80–4.62 (m, 1 H), 4.55 (s, 2 H minor), 4.49 (d, 1 H major, *J* = 11.9 Hz), 4.37 (d, 1 H major, *J* = 11.9 Hz), 3.59 (dd, 1 H minor, *J* = 9.8, 4.7 Hz), 3.51 (dd, 1 H minor, *J* = 9.8, 5.1 Hz), 3.47 (dd, 1 H major, *J* = 9.9, 3.0

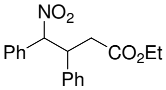
Hz), 3.17 (dd, 1 H major, *J* = 9.9, 3.9 Hz), 2.87 (d, 1 H major, *J* = 7.5 Hz), 2.55 (d, 1 H minor, *J* = 5.7 Hz);

^{13}C NMR (75 MHz, $CDCl_3$) δ 137.0, 136.8, 131.2, 131.0, 130.0, 129.7, 128.9, 128.9, 128.6, 128.3, 128.2, 127.8, 127.7, 127.6, 93.5, 90.4, 73.5, 73.4, 72.0, 70.3, 69.8, 69.1;

FTIR (KBr, cm^{-1}) ν 3352, 1557, 1456, 1373;

EA calcd for $C_{16}H_{17}NO_4$ C 66.89, H 5.96, N 4.88. Found C 66.97, H 5.92, N 4.80.

ethyl 4-nitro-3,4-diphenylbutanoate (22)



Prepared following conditions given in Scheme B;

Colourless solid; mp. 96-111 °C; mixture of two diastereoisomers;

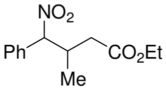
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70-7.00 (m, 10 H), 5.79 (d, 1 H major, *J* = 12.0 Hz), 5.70 (d, 1 H minor, *J* = 11.1 Hz), 4.32-4.20 (m, 1 H), 4.04-3.92 (m, 2 H minor), 3.87 (d, 2 H major, *J* = 7.1 Hz), 2.88 (dd, 1 H minor, *J* = 15.5, 9.9 Hz), 2.78 (dd, 1 H minor, *J* = 15.5, 4.6 Hz), 2.47 (dd, 1 H major, *J* = 15.5, 9.8 Hz), 2.35 (dd, 1 H major, *J* = 15.5, 4.5 Hz), 1.07 (t, 3 H minor, *J* = 7.4 Hz), 1.01 (t, 3 H major, *J* = 7.1 Hz);

^{13}C NMR (75 MHz, $CDCl_3$) δ 170.2, 137.9, 136.7, 132.5, 132.4, 130.3, 129.6, 129.2, 128.7, 128.5, 128.4, 128.3, 128.2, 128.1, 127.9, 127.8, 127.4, 95.4, 95.0, 60.7, 60.7, 46.0, 45.8, 38.2, 37.6, 14.0, 14.0;

FTIR (KBr, cm^{-1}) ν 1729, 1551, 1456, 1366;

EA calcd for $C_{18}H_{19}NO_4$ C 69.00, H 6.11, N 4.47. Found C 68.85, H 6.22, N 4.42.

ethyl 3-methyl-4-nitro-4-phenylbutanoate (24)



Prepared following conditions given in Scheme B;

Colourless oil; mixture of two diastereoisomers;

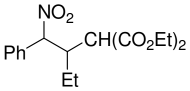
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55–7.37 (m, 5 H), 5.39 (d, 1 H major, *J* = 11.1 Hz), 5.37 (d, 1 H minor, *J* = 11.1 Hz), 4.17 (q, 2 H minor, *J* = 7.2 Hz), 4.06 (q, 2 H major, *J* = 7.2 Hz), 3.18–3.04 (m, 1 H), 2.50 (dd, 1 H minor, *J* = 15.8, 3.8 Hz), 2.34 (dd, 1 H minor, *J* = 15.8, 8.4 Hz), 2.17 (dd, 1 H major, *J* = 15.8, 4.1 Hz), 2.00 (dd, 1 H major, *J* = 15.8, 8.4 Hz), 1.28 (t, 3 H minor, *J* = 7.2 Hz), 1.21 (t, 3 H major, *J* = 7.2 Hz), 1.18 (d, 3 H major, *J* = 6.0 Hz), 0.84 (d, 3 H minor, *J* = 6.9 Hz);

^{13}C NMR (75 MHz, $CDCl_3$) δ 171.0, 170.9, 133.1, 132.9, 130.0, 129.9, 129.0, 128.9, 128.2, 128.0, 96.2, 95.5, 60.7, 60.7, 37.9, 37.0, 34.4, 34.2, 17.0, 15.9, 14.3, 14.2;

FTIR (thin film, cm^{-1}) ν 1732, 1556, 1456, 1362;

EA calcd for $C_{13}H_{17}NO_4$ C 62.14, H 6.82, N 5.57. Found C 62.35, H 7.02, N 5.50.

diethyl 2-(1-nitro-1-phenylbutan-2-yl)malonate (26)



Prepared following conditions given in Scheme B;

Colourless oil; mixture of diastereoisomers;

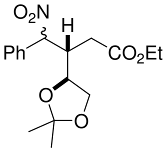
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56–7.34 (m, 5 H), 5.84 (d, 1 H major, *J* = 11.1 Hz), 5.76 (d, 1 H minor, *J* = 11.1 Hz), 4.31–3.85 (m, 4 H), 3.56 (d, 1 H minor, *J* = 3.6 Hz), 3.31–3.13 (m, 1 H minor and 2 H major), 1.82–1.44 (m, 2 H), 1.35–1.14 (m, 6 H), 1.00 (t, 3 H major, *J* = 7.5 Hz), 0.63 (t, 3 H minor, *J* = 7.7 Hz);

^{13}C NMR (75 MHz, CDCl$_3$) δ 168.0, 167.9, 167.7, 167.4, 133.3, 132.6, 130.1, 129.9, 128.9, 128.8, 128.6, 128.2, 128.2, 94.2, 93.1, 61.8, 61.7, 61.4, 52.0, 51.3, 43.4, 43.2, 23.2, 21.8, 14.1, 14.1, 14.0, 12.7, 12.4;

FTIR (thin film, cm^{-1}) ν 1755, 1748, 1738, 1732, 1557, 1457, 1368;

EA calcd for C$_{17}$H$_{23}$NO$_6$ C 60.52, H 6.87, N 4.15. Found C 60.73, H 6.86, N 4.16.

(*S*)-ethyl 3-((*S*)-2,2-dimethyl-1,3-dioxolan-4-yl)-4-nitro-4-phenyl butanoate (28)



Prepared following conditions given in Scheme B;

Colourless solid; mp. 65–72 °C; mixture of diastereoisomers;

^{1}H NMR (300 MHz, CDCl$_3$) δ 7.52–7.37 (m, 5 H), 5.73 (d, 1 H minor, *J* = 7.5 Hz), 5.69 (d, 1 H major, *J* = 9.9 Hz), 4.21–3.95 (m, 3 H minor and 4 H major), 3.85–3.73 (m, 1 H major and 1 H minor), 3.60–3.30 (m, 2 H minor and 1 H major), 2.52–2.47 (m, 2 H minor), 2.15 (d, 2 H major, *J* = 5.4 Hz); 1.41 (s, 3 H major), 1.39 (s, 3 H minor), 1.34 (s, 3 H major), 1.26 (s, 3 H minor), 1.24 (t, 3 H minor, *J* = 7.1 Hz), 1.17 (t, 3 H major, *J* = 7.2 Hz);

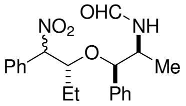
^{13}C NMR (75 MHz, CDCl$_3$) δ 171.3, 170.7, 132.5, 132.4, 129.9, 129.7, 129.0, 128.9, 128.4, 127.8, 109.7, 109.3, 91.7, 91.1, 76.2, 74.9, 67.3, 66.2, 60.9, 41.8, 41.2, 32.4, 31.9, 26.2, 25.8, 25.3, 25.1, 14.1;

FTIR (KBr, cm^{-1}) ν 1721, 1547, 1374;

EA calcd for C$_{17}$H$_{23}$NO$_6$ C 60.52, H 6.87, N 4.15. Found C 60.54, H 6.99, N 4.17;

[α]$_D^{24}$ (C=0.50, CHCl$_3$): −8.1.

***N*-((1*R*,2*S*)-1-((*R*)-1-nitro-1-phenylbutan-2-yloxy)-1-phenylpropan-2-yl)formamide (34)**



Prepared following the procedure reported by Enders.[7] The starting nitro-alkene was prepared following conditions given in Scheme A; Colourless paste; mixture of diastereoisomers and rotamers (*a*-15:*b*-5:*c*-3:*d*-1);

^{1}H NMR (300 MHz, CDCl$_3$) δ 8.16 (s, 1 H *c*), 8.06 (s, 1 H *a*), 7.86 (d, 1 H *d*, *J* = 11.7 Hz), 7.80 (d, 1 H *b*, *J* = 11.7 Hz), 7.50-6.70 (m, 10 H), 5.94-5.84 (m, 1 H *c*), 5.63-5.44 (m, 2 H *a*, 1 H *b*, 1 H *c*, 1 H *d*), 5.40-5.20 (m, 1 H *b* and 1 H *d*), 4.72 (d, 1 H *c*, *J* = 3.3 Hz), 4.55 (d, 1 H *a*, *J* = 3.6 Hz), 4.50-4.10 (m, 2 H), 3.76-3.58 (m, 1 H *b* and 1 H *d*), 1.80-1.57 (m, 2 H), 1.10-0.77 (m, 6 H);

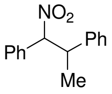
^{13}C NMR (75 MHz, CDCl$_3$) δ 163.4, 160.1, 160.1, 136.5, 136.4, 135.3, 131.5, 131.1, 130.2, 130.0, 129.6, 129.3, 129.1, 128.9, 128.4, 128.3, 128.1, 128.0, 127.7, 127.4, 127.2, 93.6, 91.2, 91.0, 81.5, 80.1, 79.0, 77.1, 76.8, 75.0, 52.6, 49.0, 48.6, 30.3, 29.7, 21.6, 21.5, 19.0, 17.5, 14.7, 13.9, 8.1, 7.8, 6.1;

FTIR (CHCl$_3$ solution, cm^{-1}) ν 3436, 1686, 1555, 1498, 1455;

LRMS (ESI) *m/z* Calculated for $C_{20}H_{24}N_2O_4Na$ 379.2, found 379.0;

$[\alpha]_D^{29}$ (C=0.1.53, CHCl$_3$): -77.1.

1,2-diphenyl-nitropropane (32)



A Schlenk tube under Argon was charged with Pd$_2$(dba)$_3$.CHCl$_3$ (25.2 mg, 0.024 mmol, 7.50 mol%), anhydrous Cs$_2$CO$_3$ (233 mg, 0.684 mmol, 220 mol%) and 2-(di-*tert*-butylphosphino)-2'-methylbiphenyl (29.5 mg, 0.950 mmol, 30.0 mol%). DME (1 mL) was added and the suspension stirred at room temperature for 15 min. A solution of bromobenzene

(52.0 μL, 150 mol%) and 2-phenylnitropropane (54.0 mg, 0.325 mmol) in DME (1 mL) was added and the Schlenk tube was sealed and heated to 55 °C for 36 h. After this time, the mixture was allowed to cool to room temperature and saturated aq. NH_4Cl was added. After extraction (CH_2Cl_2), the combined organic layers were dried ($MgSO_4$), filtered and evaporated *in vacuo*. Crude ^{1}H-NMR showed 90% conversion. The residue was passed through a short silica column, eluted with *n*-pentane-diethyl ether 50:1 to afford a mixture of desired product and ligand, which was used in the next reaction. A small amount of pure desired product could be isolated for characterization purposes.

White solid; mp. 86-87 °C; mixture of two diasteroisomers;
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68-7.01 (m, 10 H), 5.62 (d, 1 H minor, *J* = 11.5 Hz), 5.59 (d, 1 H major, *J* = 11.2 Hz), 3.95-3.82 (m, 1 H), 1.49 (d, 3 H major, *J* = 6.5 Hz), 1.10 (d, 3 H minor, *J* = 7.2 Hz);
^{13}C NMR (75 MHz, $CDCl_3$) δ 130.0, 129.4, 129.0, 128.8, 128.5, 128.1, 127.6, 127.5, 127.1, 127.0, 97.4, 44.4, 44.0, 19.8, 18.8;
FTIR (thin film, cm^{-1}) ν 3064, 3032, 2475, 2935, 1551, 1496, 1454, 1361, 761, 722, 696;
EA calcd for $C_{16}H_{17}NO_2$ C 75.27, H 6.71, N 5.49. Found C 75.24, H 6.81, N 5.37.

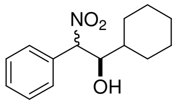
Conjugate addition of trialkylaluminium species to nitrostilbene:
A solution of CuTC (5 mol%) and ligand (12.5 mol%) in dry Et_2O (5 mL) was stirred at room temperature for 45 min. A solution of nitrostilbene (100 mg) in Toluene (1 mL) was added and the reaction mixture was cooled to −78 °C. The solution of trialkylaluminium in Hexanes (2.5 eq) was added dropwise and the reaction mixture stirred at −78 °C for 48 h. A solution of saturated NH_4Cl was slowly added and the mixture was extracted with Et_2O. The combined organic

layers and were dried ($MgSO_4$), filtered and the solvent was evaporated *in vacuo*. Purification of the residue by column chromatography (*n*-pentane-diethyl ether 50:1) afforded the desired nitro compounds **1** and **32** in resp. 74% (87 mg) and 72% (76 mg) yield.

Enantioselective Henry-aldol reaction:

To a mixture of phenylnitromethane (98 mg, 0.71 mmol) and (*S*,*S*)-guanidine-thiourea catalyst[8] (41 mg, 0.036 mmol) in toluene (4 mL) was added an aqueous KOH solution (4 mL of 4.5 mM in water, 0.018 mmol) and the reaction mixture was stirred for 30 min at room temperature. Then most of the aqueous layer was removed with a syringe. The remaining toluene solution was cooled down to −40 °C, and cyclohexanecarboxaldehyde (36 μL, 0.36 mmol) was slowly added to this toluene solution. After stirring for 24 h at −40 °C, the reaction was quenched with saturated NH_4Cl solution, extracted with EtOAc, washed with brine and dried with $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography (hexanes-EtOAc 20:1 -10:1 then dichloromethane-methanol 9:1) to give alcohol **30** as a colorless solid (17.4 mg, 20%). At this stage, the exact enantio purity of the product was not determined.

1-cyclohexyl-2-nitro-2-phenylethanol (30)

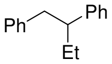


^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51-7.36 (m, 5 H), 5.53 (d, 1 H, *J* = 9.9 Hz), 4.48-4.38 (m, 1 H), 2.25 (br d, 1 H , *J* = 5.1 Hz), 1.76-0.80 (m, 11 H).

General procedure for the reductive cleavage of benzylic nitro groups:

The palladium catalyst was added to a suspension of substrate in the designated solvent. The resulting suspension was heated to temperature T and the atmosphere replaced by H_2 (1 bar, balloon) by two pump-H_2 cycles. The reaction mixture was then stirred vigorously at T under an atmosphere of H_2. When the reaction was complete as judged by disappearance of the substrate by TLC analysis, the reaction mixture was cooled to RT and H_2 was replaced by Argon (two vacuum-Ar cycles). The suspension was diluted with dichloromethane and filtered through a plug of Celite®. The pad was washed with dichloromethane and the filtrate was evaporated *in vacuo* to afford the crude product. Conversion and ratio product:amine were determined by ^{1}H-NMR of this crude mixture. Purification of the residue by flash column chromatography (Cyclohexane-Ethyl acetate) afforded the cleavage products in indicated yields.

1,2-diphenylbutane (2)



Obtained from **1** using general procedure with 5 mol% $Pd(OH)_2/C$ in EtOH, at 70 °C;

Colourless oil;

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33-7.05 (m, 10 H), 2.92 (d, 2 H, J = 7.5 Hz), 2.81-2.69 (m, 1 H), 1.85-1.56 (m, 2 H), 0.80 (t, 3 H, J = 7.5 Hz);

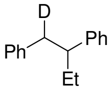
^{13}C NMR (75 MHz, $CDCl_3$) δ 144.9, 140.8, 129.1, 128.1, 127.9, 127.7, 125.9, 125.6, 49.9, 43.6, 28.4, 12.3;

FTIR (thin film, cm^{-1}) ν 3084, 3062, 3027, 2961, 2928, 2874, 1602, 1495, 1452, 1378, 1066, 1030, 757, 731, 698;

HRMS (EI) *m/z* calculated for $C_{16}H_{18}$ ($[M]^+$) 210.1404, found 210.1405.

HPLC (OJ-H 25cm, *n*-hexane/*i*-PrOH 99/1 215nm, 0.5mL/min): 11.0 (R), 16.1 (S). 77% *ee* (*R*) using conditions in [Eq. (4)].

1-*d*-1,2-diphenylbutane (*d*-2)



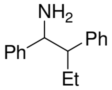
Obtained from **1** using general procedure with 5 mol% Pd/C in CD_3OD, at 60 °C;

Colourless oil;

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34-7.05 (m, 10 H), 2.94-2.87 (m, 1.09 H), 2.81-2.70 (m, 1 H), 1.85-1.56 (m, 2 H), 0.81 (t, 3 H, J = 7.2 Hz);

^{13}C NMR (75 MHz, $CDCl_3$) δ 144.9, 140.7, 129.0, 128.1, 127.9, 127.7, 125.9, 125.6, 49.9 (d), 43.6 (m), 28.4, 12.3.

1,2-diphenylbutylamine (3)



Obtained from **1** using general procedure with 5 mol% $Pd(OH)_2/C$ in EtOH, at 0 °C. (1:1 mixture with **2**);

Colourless oil; mixture of diastereoisomers;

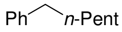
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42-6.96 (m, 10 H), 4.11 (s, 1 H, minor, J = 6.5 Hz), 4.03 (d, 1 H major, J = 9.0 Hz), 2.85-2.74 (m 1 H major), 2.68-2.57 (m, 1 H minor), 1.97-1.83 (m, 1 H), 1.79-1.62 (m, 1 H), 1.48-1.34 (m, 4 H), 0.76 (t, 3 H major, J = 7.2 Hz), 0.59 (t, 3 H minor, J = 7.5 Hz);

^{13}C NMR (75 MHz, $CDCl_3$) δ 144.8, 144.4, 142.4, 141.6, 128.8, 128.5, 128.4, 128.3, 127.8, 127.7, 127.4, 127.1, 126.5, 126.5, 126.1, 61.7, 61.1, 56.4, 55.6, 26.0, 23.4, 12.4, 12.3;

FTIR (thin film, cm^{-1}) ν 3373, 3061, 3027, 2961, 2930, 2873, 1602, 1494, 1452, 1378, 1072, 1027, 765;

HRMS (MALDI) *m/z* calculated for $C_{16}H_{19}N$ ($[M+H]^+$) 226.1590, found 226.1590.

Hexylbenzene (5)[9]



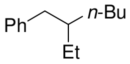
Obtained from **4** using general procedure with 10 mol% $Pd(OH)_2/C$ in EtOH, at 70 °C.

Colourless liquid;

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32–7.14 (m, 5 H), 2.61 (t, 2 H, *J* = 7.4 Hz), 1.68–1.52 (m, 2 H), 1.41–1.24 (m, 6 H), 0.89 (t, 3 H, *J* = 6.6 Hz);

^{13}C NMR (75 MHz, $CDCl_3$) δ 142.9, 128.3, 128.1, 125.4, 77.3, 76.9, 76.5, 35.9, 31.6, 31.4, 28.9, 22.5, 14.0.

(2-ethylhexyl)benzene (7)



Obtained from **6** using general procedure with 10 mol% $Pd(OH)_2/C$ in EtOH, at 70 °C;

Colourless oil;

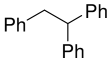
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32–7.12 (m, 5 H), 2.53 (d, 2 H, *J* = 7.2 Hz), 1.64–1.51 (m, 1 H), 1.36–1.22 (m, 8 H), 0.88 (t, 6 H, *J* = 7.5 Hz);

^{13}C NMR (75 MHz, $CDCl_3$) δ 141.8, 129.1, 127.9, 125.4, 41.0, 40.0, 32.2, 28.7, 25.3, 22.9, 14.0, 10.7;

FTIR (thin film, cm^{-1}) ν 3061, 2964, 2931, 2860, 1605, 1500, 1450, 1379, 1031, 740;

HRMS (EI) calculated for $C_{14}H_{22}$ ($[M]^+$) 190.1717, found 190.1720.

1,1,2-triphenylethane (9)



Obtained from **8** using general procedure with 10 mol% $Pd(OH)_2/C$ in EtOH, at 70 °C.

Colourless oil;

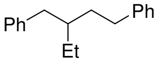
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29-7.12 (m, 13 H), 7.04-6.99 (m, 2 H), 4.24 (t, 1 H, *J* = 7.7 Hz), 3,37 (d, 1 H, *J* = 7.7 Hz),

^{13}C NMR (75 MHz, $CDCl_3$) δ 144.4, 140.2, 129.0, 128.2, 128.0, 126.1, 125.8, 53.0, 42.0;

FTIR (thin film, cm^{-1}) ν 3062, 3027, 2926, 2360, 1602, 1495, 1452, 1070, 1031, 751, 733, 697;

HRMS (EI) calculated for $C_{20}H_{18}$ ($[M]^+$) 258.1404, found 258.1403.

2-benzyl-1-phenylpentane (11)



Obtained from **10** using general procedure with 10 mol% $Pd(OH)_2/C$ in EtOH, at 70 °C;

Colourless oil;

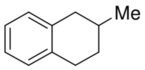
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37-7.12 (m, 10 H), 2.70-2.54 (m, 4 H), 1.74-1.56 (m, 2 H), 1.45-1.32 (m, 2 H), 0.93 (t, 3 H, *J* = 7.4 Hz);

^{13}C NMR (75 MHz, $CDCl_3$) δ 143.1, 141.7, 129.4, 128.5, 128.5, 128.3, 125.8, 125.8, 40.9, 40.2, 34.8, 33.2, 25.6, 10.9;

FTIR (thin film, cm^{-1}) ν 3062, 3026, 2960, 2927, 2858, 1602, 1495, 1454, 1379, 1030, 733, 698;

HRMS (EI) *m/z* calculated for $C_{18}H_{22}$ ($[M]^+$) 238.1718, found, 238.1717.

2-methyl-1,2,3,4-tetrahydronaphtalene (13)[10]



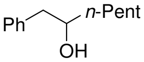
Obtained from **12** using general procedure with 5 mol% Pd(OH)$_2$/C in EtOH, at 70 °C;

Colourless liquid;

^{1}**H NMR** (300 MHz, CDCl$_3$) δ 7.10-7.04 (m, 4 H), 2.87-2.77 (m, 4 H), 2.40 (dd, 1 H, *J* = 16.8, 10.6 Hz), 1.95-60 (m, 3 H), 1.06 (d, 3 H, *J* = 6.5 Hz);

^{13}**C NMR** (75 MHz, CDCl$_3$) δ 136.9, 136.6, 129.0, 128.8, 125.4, 125.4, 38.3, 31.7, 29.4, 29.4, 22.2.

1-phenylheptan-2-ol (15)



Obtained from **14** using general procedure with 5 mol% Pd(OH)$_2$/C in EtOH, at 70 °C;

Colourless oil;

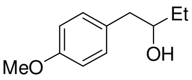
^{1}**H NMR** (300 MHz, CDCl$_3$) δ 7.37-7.19 (m, 5 H), 3.87-3.46 (m, 1 H), 2.84 (dd, 1 H, *J* = 13.7, 4.4 Hz), 2.65 (dd, 1 H, *J* = 13.5, 8.2 Hz), 1.55-1.25 (m, 10 H), 0.90 (t, 3 H, *J* = 6.6 Hz);

^{13}**C NMR** (75 MHz, CDCl$_3$) δ 138.6, 129.3, 128.5, 126.3, 72.6, 44.0, 36.7, 31.8, 25.4, 22.6, 14.0;

FTIR (thin film, cm^{-1}) ν 3370, 3028, 2929, 2858, 1596, 1454, 1125, 1081, 1032, 745, 700;

HRMS (EI) *m/z* calculated for $C_{13}H_{20}O$ ([M]$^+$) 192.1509, found 192.1508.

1-(4-methoxyphenyl)butan-2-ol (17)



Obtained from **16** using general procedure with 10 mol% Pd(OH)$_2$/C in EtOH, at 70 °C;

Colourless oil;

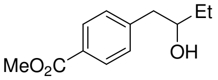
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.14 (d, 2 H, *J* = 8.7 Hz), 6.86 (d, 2 H, *J* = 8.7 Hz), 3.80 (s 3 H), 3.75–3.64 (m, 1 H), 2.79 (dd, 1 H, *J* = 13.7, 4.3 Hz), 2.59 (dd, 1 H, *J* = 13.7, 8.4 Hz), 1.63–1.44 (m, 2 H), 1.00 (t, 3 H, *J* = 7.2 Hz);

^{13}C NMR (75 MHz, $CDCl_3$) δ 158.1, 130.5, 130.3, 113.9, 74.1, 55.3, 42.7, 29.6, 10.2;

FTIR (thin film, cm^{-1}) ν 3371, 2959, 2932, 2360, 1612, 1584, 1511, 1463, 1300, 1244, 1178, 1111, 1036, 975, 808, 630;

HRMS (EI) *m/z* calculated for $C_{18}H_{22}$ ($[M]^+$) 180.1145, found 180.1145.

methyl 4-(2-hydroxybutyl)benzoate (19)



Obtained from **18** using general procedure with 10 mol% $Pd(OH)_2/C$ in EtOH, at 70 °C;

Colourless oil;

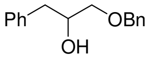
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95 (d, 2 H, *J* = 8.1 Hz), 7.27 (d, 2 H, *J* = 8.1 Hz), 3.88 (s, 3 H), 3.80–3.70 (m, 1 H), 2.84 (dd, 1 H, *J* = 13.4, 4.4 Hz), 2.70 (dd, 1 H, *J* = 13.7, 5.6 Hz), 1.77 (d, 1 H, *J* = 3.1 Hz), 1.61–1.41 (m, 2 H), 0.97 (t, 3 H, *J* = 7.5 Hz);

^{13}C NMR (75 MHz, $CDCl_3$) δ 167.2, 144.6, 129.9, 129.6, 128.5, 74.0, 52.2, 29.9, 10.2;

FTIR (thin film, cm^{-1}) ν 3422, 2929, 2876, 2361, 1715, 1611, 1575, 1435, 1276, 1179, 1105, 1021, 976, 760, 706, 631;

EA calcd for $C_{12}H_{16}O_3$ C 69.21, H 7.74. Found C 69.47, H 8.02.

1-(benzyloxy)-3-phenylpropan-2-ol (21)



Obtained from **20** using general procedure with 5 mol% Pd(OH)$_2$/C in *i*-PrOH, at 65 °C;

Colourless oil;

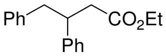
^{1}H NMR (300 MHz, CDCl$_3$) δ 7.40-7.19 (m, 10 H), 4.56 (s, 2 H), 4.11-4.02 (m, 1 H), 3.52 (dd, 1 H, *J* = 9.6, 3.3 Hz), 3.41 (dd, 1 H, *J* = 9.6, 6.9 Hz), 2.82 (d, 2 H, *J* = 6.9 Hz), 2.33 (br.s, 1 H);

^{13}C NMR (75 MHz, CDCl$_3$) δ 137.8, 137.8, 129.2, 128.3, 127.6, 126.3, 73.5, 73.3, 71.4, 39.9;

FTIR (thin film, cm^{-1}) ν 3444, 1496, 1454, 1097, 744, 699;

HRMS (EI) *m/z* calculated for $C_{16}H_{18}O_2$ ([M]$^+$) 242.1302, found 242.1303.

ethyl 3,4-diphenylbutanoate (23)



Obtained from **22** using general procedure with 4 mol% Pd(OH)$_2$/C in EtOH, at 65 °C;

Colourless oil;

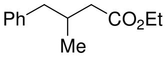
^{1}H NMR (300 MHz, CDCl$_3$) δ 7.30-7.02 (m, 10 H), 3.98 (q, 2 H, *J* = 7.1 Hz), 3.47-3.36 (m, 1 H), 2.98-2.85 (m, 2 H), 2.67 (dd, 1 H, *J* = 15.4, 6.8 Hz), 2.60 (dd, 1 H, *J* = 15.4, 8.4 Hz), 1.11 (t, 3 H, *J* = 7.1 Hz);

^{13}C NMR (75 MHz, CDCl$_3$) δ 172.0, 143.3, 139.4, 129.1, 128.2, 128.0, 127.4, 126.4, 126.0, 60.2, 44.0, 43.0, 40.3, 14.2;

FTIR (thin film, cm^{-1}) ν 1732, 1496, 1454;

HRMS (EI) *m/z* calculated for $C_{18}H_{20}O_2$ ([M]$^+$) 268.1458, found 268.1457.

ethyl 3-methyl-4-phenylbutanoate (25)



Obtained from **24** using general procedure with 4 mol% $Pd(OH)_2/C$ in *i*-PrOH, at 65 °C;

Colourless oil;

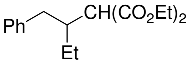
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32-7.14 (m, 5 H), 4.11 (q, 2 H, *J* = 7.1 Hz), 2.64 (dd, 1 H, *J* = 13.3, 6.3 Hz), 2.50 (dd, 1 H, *J* = 13.3, 7.1 Hz), 2.36-2.22 (m, 2 H), 2.20-2.08 (m, 1 H), 1.25 (t, 3 H, *J* = 7.1 Hz), 0.95 (d, 3 H, *J* = 6.6 Hz);

^{13}C NMR (75 MHz, $CDCl_3$) δ 172.9, 140.1, 129.1, 128.1, 125.9, 60.2, 43.1, 41.2, 32.4, 19.7, 14.4;

FTIR (thin film, cm^{-1}) ν 1733, 1455, 1372;

HRMS (EI) *m/z* calculated for $C_{13}H_{18}O_2$ ($[M]^+$) 206.1302, found 206.1302.

diethyl 2-(1-phenylbutan-2-yl)malonate (27)



Obtained from **26** using general procedure with 10 mol% $Pd(OH)_2/C$ in EtOH, at 70 °C;

Colourless oil;

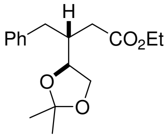
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32-7.16 (m, 5 H), 4.25-4.13 (m, 4 H), 3.44 (d, 1 H, *J* = 6.6 Hz), 2.74 (dd, 1 H, *J* = 13.8, 6.5 Hz), 2.65 (dd, 1 H, *J* = 13.8, 8.0 Hz), 2.44-2.33 (m, 1 H), 1.49-1.34 (m, 2 H), 1.32-1.23 (m, 6 H), 0.92 (t, 3 H, *J* = 7.5 Hz);

^{13}C NMR (75 MHz, $CDCl_3$) δ 168.8, 140.1, 129.2, 128.2, 126.0, 61.2, 54.1, 41.9, 37.2, 23.4, 14.2, 14.2, 11.2;

FTIR (thin film, cm^{-1}) ν 1755, 1748, 1738, 1732, 1455;

HRMS (EI) *m/z* calculated for $C_{17}H_{24}O_4$ 292.1670, found 292.1672.

(*R*)-ethyl 3-((*S*)-2,2-dimethyl-1,3-dioxolan-4-yl)-4-phenylbutanoate (29)



Obtained from **28** using general procedure with 6 mol% Pd(OH)$_2$/C in *i*-PrOH, at 70 °C;

Colourless oil;

^{1}H NMR (300 MHz, CDCl$_3$) δ 7.32-7.17 (m, 5 H), 4.12-4.02 (m, 3 H), 3.99 (dd, 1 H, *J* = 8.0, 6.5 Hz), 3.71-3.65 (m, 1 H), 2.79 (dd, 1 H, *J* = 13.7, 5.7 Hz), 2.66 (dd, 1 H, *J* = 13.7, 8.1 Hz), 2.56-2.44 (m, 1 H), 2.33 (dd, 1 H, *J* = 15.8, 6.2 Hz), 2.19 (dd, 1 H, *J* = 15.8, 6.8 Hz), 1.44 (s, 3 H), 1.34 (s, 3 H), 1.23 (t, 3 H, *J* = 7.2 Hz);

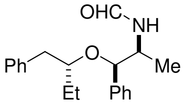
^{13}C NMR (75 MHz, CDCl$_3$) δ 172.4, 138.9, 129.2, 128.3, 126.1, 108.8, 76.8, 66.6, 60.4, 39.6, 36.4, 34.3, 26.5, 25.3, 14.3□

FTIR (thin film, cm^{-1}) ν 1732, 1455, 1371;

HRMS (EI) *m/z* calculated for $C_{16}H_{21}O_4$ ($[M-CH_3]^+$) 277.1435, found 277.1434;

[α]$_D^{26}$ (C=0.74, CHCl$_3$): -3.1.

N-((1*R*,2*S*)-1-phenyl-1-((*R*)-1-phenylbutan-2-yloxy)propan-2-yl)formamide (35)



Obtained from **34** using general procedure with 10 mol% Pd(OH)$_2$/C in EtOH, at 65 °C;

Colourless oil; mixture of rotamers;

^{1}H NMR (300 MHz, CDCl$_3$) δ 8.16 (d, 1 H major, *J* = 0.9 Hz), 8.00 (d, 1 H minor, *J* = 11.7 Hz), 7.33-7.05 (m, 8 H), 6.91-6.78 (m, 2 H), 5.83 (br. d, 1 H major, *J* = 8.1 Hz), 5.44 (br. t, 1 H minor, *J* = 10.8 Hz), 4.60 (d, 1 H major, *J* = 3.3 Hz), 4.35 (d, 1 H minor, *J* =

4.2 Hz), 4.28–4.16 (m, 1 H major), 3.74–3.61 (m, 1 H minor), 3.47–3.36 (m, 1 H), 2.82–2.67 (m, 2 H), 1.66–1.44 (m, 2 H), 1.05 (d, 3H minor, J = 6.9 Hz), 0.98–0.91 (m, 3H minor and 6 H major);

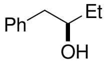
^{13}C NMR (75 MHz, $CDCl_3$) δ 163.8, 160.2, 139.1, 139.0, 138.8, 137.5, 129.8, 129.7, 128.2, 128.1, 127.9, 127.6, 127.4, 127.0, 126.1, 81.1, 79.5, 78.5, 78.3, 52.8, 48.9, 40.4, 24.5, 16.9, 13.8, 9.0, 8.8

FTIR (thin film, cm^{-1}) ν 3292, 1686, 1655, 1493, 1452;

HRMS (MALDI) *m/z* calculated for $C_{20}H_{26}NO_2$ ($[M+H]^+$) 312.1958, found 312.1971;

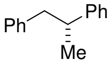
$[\alpha]_D^{24}$ (C=1.11, $CHCl_3$): –76.0.

(*R*)-1-phenylbutan-2-ol (36)



For analytical purposes, **35** was treated under conditions reported by Enders and afford the corresponding alcohol **36** with >99% ee,[7] as determined by HPLC (OD-H 25cm, *n*-hexane/*i*-PrOH 97/3, 254nm, 0.5mL/min): 14.2 (*S*), 17.8 (*R*); *99.2% ee* (*R*).[11]

(*R*)-1,2-diphenylpropane (33)[12]



Obtained from **32** using general procedure with 5 mol% $Pd(OH)_2/C$ in EtOH, at 70 °C;

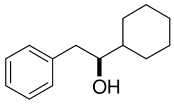
Colourless oil;

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34–7.08 (m, 10 H), 3.08–2.92 (m, 2 H), 2.84–2.72 (m, 1 H), 1.26 (d, 3 H, J = 6.6 Hz);

^{13}C NMR (75 MHz, $CDCl_3$) δ 146.9, 140.7, 129.1, 128.2, 128.0, 126.9, 125.9, 125.7, 44.9, 41.8, 21.0;

HPLC (OJ-H 25cm, *n*-hexane/*i*-PrOH 99/1 215nm, 0.5mL/min): 12.1 (*R*), 17.2 (*S*); *87% ee* (*R*) using conditions in [Eq. (3)]; *95% ee* (*R*) using conditions in [Eq. (4)].

(*S*)-benzylcyclohexylmethanol (31)[13]



Obtained from **30** using general procedure with 10 mol% $Pd(OH)_2/C$ in EtOH, at 65 °C;

Colorless solid;

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36-7.19 (m, 5 H), 3.63-3.54 (m, 1 H), 2.89 (dd, 1 H, *J* = 3.5, 13.7 Hz), 2.60 (dd, 1 H, *J* = 9.3, 13.7 Hz), 1.92 (br d, 1 H, *J* = 12.0 Hz), 1.85-1.00 (m, 11 H);

HPLC (OD-H 25cm, *n*-hexane/*i*-PrOH = 99:1, 210 nm, 0.8 mL/min): 11.5 min (*R*), 15.2 min (*S*); *94% ee* (*S*).

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