Supplementary Information

Improving catalyst activity in secondary amine catalysed transformations


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Contents

General Techniques .................................................. S3
Experimental Procedures and Analytical Data .................. S4
Determination of Enantiomeric Excess .......................... S17
General Method for Calculating PA of catalysts .......... S20
Preparation and Table of X-Ray Data for Isolated Iminium Ion S21
$^1$H and $^{13}$C NMR Spectra and HPLC Chromatograms .... S23
References .............................................................. S36
**General Techniques**

Reagents and solvents were purchased from Sigma Aldrich, Alfa Aesar, Fisher Scientific or Fluorochem and were used as received. Flash chromatography was performed using Merck Kieselgel 60 H silica. Analytical thin layer chromatography was carried out using aluminium-backed plates coated with Merck Kieselgel 60 GF254. Depending on compound functionality, TLC plates were visualized using either UV light (254 nm), a basic KMnO₄ dip or an acidic ethanolic 2,4-dinitrophenylhydrazine dip. Nuclear magnetic resonance (NMR) spectra were recorded at 300 K on a Bruker Avance III 400 MHz or Bruker Avance DRX 500 MHz. All spectra were referenced internally to residual solvent signals. J values were reported in hertz and multiplicities were expressed using usual conventions. Low-resolution mass spectra (MS) were determined on an Agilent 6130 single quadrupole with an APCI/electrospray dual source or ThermoQuest Finnigan LCQ DUO electrospray. High-resolution mass spectra were obtained courtesy of the EPSRC National Mass Spectrometry Facility at Swansea University, Swansea, UK. Infra-red spectra were recorded in the range 4000–600 cm⁻¹ on a Shimadzu IRAffinity-1 equipped with an ATR accessory. Melting points were determined on a Stuart SMP11 and were measured to the nearest 1 °C. Optical rotations were recorded on a PerkinElmer 341 polarimeter. GCMS analysis was performed using an Agilent 7890A GC system, equipped with a 30 m DB5MS column connected to a 5975C inert XL CI MSD with Triple-Axis Detector or Thermo Finnigan Polaris Q equipped with an Agilent DB-5MS UI column connected to an EI MSD. HPLC was performed on an Agilent 1200 series system equipped with an auto mixer, auto sampler, column oven and variable wavelength detector. Single-crystal diffraction data was obtained using an Oxford Diffraction Xcalibur E or Gemini S instrument. The structures were refined to convergence on $R^2$ and against all independent reflections by full-matrix least-squares, using the SHELXL-97 program.¹ Selected parameters are given on page S18 and full details are given in the deposited cif files (CCDC 1017471). This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).
**Experimental Procedures and Analytical Data**

**L-Phenylalanine N-methyl amide 18**

L-Phenylalanine ethyl ester hydrochloride (30.0 g, 131 mmol) was stirred in an ethanolic solution of methylamine 33 wt.% (150 mL, 1.2 mol) for 72 hours at ambient temperature. The solvent was removed under reduced pressure. The resultant slurry was taken up in saturated sodium carbonate (50 mL) and extracted with chloroform (3 × 50 mL). The combined organic extracts were dried over anhydrous potassium carbonate and the solvent removed under reduced pressure to give a white solid. The residue was recrystallized from ethyl acetate and petroleum ether to give the product as white needles (17.6 g, 75%). m.p: 67–69 °C; [α]_D^{20} = -89.6 (c=1, CHCl₃); ν<sub>max</sub> (film)/cm⁻¹ 3371, 3345, 3290, 2939, 2875, 1644; ¹H NMR (400 MHz, CDCl₃) δ 7.47–7.12 (6H, m), 3.54 (1H, dd, J = 9.5, 3.9 Hz), 3.22 (1H, dd, J = 13.7, 3.9 Hz), 2.83 (3H, d, J = 5.0 Hz), 2.60 (1H, dd, J = 13.7, 9.5 Hz), 1.38 (2H, s); ¹³C NMR (101 MHz, CDCl₃) δ 174.8, 138.0, 129.3, 128.7, 126.8, 56.5, 41.0, 25.8; m/z (ES): 179.1 (M+H⁺).

**(S)-5-Benzyl-2,2,3-trimethylimidazolidin-4-one 13**

L-Phenylalanine-N-methyl amide (2.00 g, 11.2 mmol) was dissolved in acetone (10 mL) and methanol (30 mL). A small crystal of p-toluenesulfonic acid (<1 mg) was added and the mixture was heated under reflux for 18 h. The solvent was removed under reduced pressure and the residue taken up in chloroform (30 mL) and saturated sodium carbonate solution (30 mL). The aqueous layer was extracted with chloroform (2 × 30 mL) and the combined organics were dried over potassium carbonate. The solvent was removed under reduced pressure to give the target compound as a pale yellow oil (2.40 g, quant.). [α]_D^{20} = -33.5 (c=1.3, MeOH); ν<sub>max</sub> (film)/cm⁻¹ 3473, 3329, 3060, 3030, 2975, 2929, 1685; ¹H NMR (400 MHz, CDCl₃) δ 7.38–7.14 (5H, m), 3.82 (1H, dd, J = 6.5, 4.5 Hz), 3.17 (1H, dd, J = 14.2, 4.5 Hz), 3.03 (1H, dd, J = 14.2, 6.5 Hz), 2.77 (3H, s), 1.28 (3H, s), 1.18 (3H, s); ¹³C NMR (126 MHz, CDCl₃) δ 173.7, 137.6, 129.9, 129.0, 127.2, 75.9, 59.7, 37.7, 27.6, 25.7, 25.6; m/z (APCI): 219.2 (M+H⁺).
General Procedure for the preparation of imidazolidinones 20–23

A toluene solution of L-Phenylalanine-\(N\)-methyl amide (0.6 M), the appropriate substituted acetophenone (0.9 eq.) and ytterbium(III) trifluoromethanesulfonate (0.05 eq.) were heated under reflux for 16–69 h. The mixture was then allowed to cool and diethyl ether (2 vol.) was added. The solution was washed with 4 M potassium carbonate (0.3 vol.), water (0.3 vol.), and brine (0.3 vol.). The volatiles were then removed under reduced pressure and the desired products obtained by flash chromatography (ethyl acetate/heptane).

\[(2R,5S)-5\text{-Benzyl}-2\text{-}(4\text{-methoxyphenyl})-2,3\text{-dimethylimidazolidin-4-one} 20\]

Prepared according to General Procedure. \([\alpha]^{20}_{D}\) (c 0.1, \(\text{CH}_2\text{Cl}_2\)); \(\nu_{\text{max}}\) (NaCl disk)/cm\(^{-1}\) 3360, 2933, 1690, 1608, 1510; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) \(H\) 7.23–7.08 (7H, m), 6.78 (2H, d, \(J = 8.9\) Hz), 3.81 (1H, dd, \(J = 7.2\) Hz, 4.2 Hz), 3.71 (3H, s), 3.08 (1H, dd, \(J = 13.9\) Hz, 4.2 Hz), 2.93 (1H, dd, \(J = 13.9\) Hz, 7.2 Hz), 2.64 (3H, s), 1.46 (3H, s); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) \(C\) 173.6, 159.4, 137.7, 134.9, 129.7, 128.5, 126.7, 126.5, 114.1, 78.4, 59.4, 55.3, 38.4, 26.4, 26.1; LRMS \(m/z\) (ES) (M+H\(^+\)) = 311.2; HRMS \(m/z\) (ES) (M+H\(^+\)) = 311.1753; HRMS \(m/z\) calc. (M+H\(^+\)) = 311.1760.
(2R,5S)-5-Benzyl-2,3-dimethyl-2-phenylimidazolidin-4-one 21

Prepared according to General Procedure. \([\alpha]_D^{30} 3.0 \ (c \ 0.1, \ \text{CH}_2\text{Cl}_2); \ \nu_{\text{max}} \ (\text{NaCl disk})/\text{cm}^{-1} 1693, 1454; ^1\text{H} \text{NMR} \ (500 \text{ MHz, CDCl}_3) \ \delta_H \ 7.23 \ (2\text{H}, \text{ t}, \ J = 6.2 \text{ Hz}), 7.20–7.09 \ (8\text{H}, \text{ m}), 3.76 \ (1\text{H}, \text{ dd}, \ J = 7.1 \text{ Hz}, 4.2 \text{ Hz}), 3.05 \ (1\text{H}, \text{ dd}, \ J = 13.9 \text{ Hz}, 4.2 \text{ Hz}), 2.91 \ (1\text{H}, \text{ dd}, \ J = 13.9 \text{ Hz}, 7.1 \text{ Hz}), 2.63 \ (3\text{H}, \text{ s}), 1.45 \ (3\text{H}, \text{ s}); ^13\text{C} \text{NMR} \ (125 \text{ MHz, CDCl}_3) \ \delta_C \ 173.7, 142.8, 137.6, 129.7, 128.9, 128.5, 128.1, 126.7, 125.1, 78.6, 59.3, 38.3, 26.3, 26.2; \ \text{LRMS} \ m/z \ (\text{ES}) \ (\text{M+H})^+ = 281.2; \ \text{HRMS} \ m/z \ (\text{ES}) \ (\text{M+H})^+ = 281.1646; \ \text{HRMS} \ m/z \ \text{calc.} \ (\text{M+H})^+ = 281.1654.

2R,5S)-5-Benzyl-2-(4-chlorophenyl)-2,3-dimethylimidazolidin-4-one 22

Prepared according to General Procedure. \([\alpha]_D^{30} 5.2 \ (c \ 0.1, \ \text{CH}_3\text{OH}); \ \nu_{\text{max}} \ (\text{NaCl disk})/\text{cm}^{-1} 3316, 2720, 1704, 1493; ^1\text{H} \text{NMR} \ (500 \text{ MHz, CDCl}_3) \ \delta_H \ 7.23–7.19 \ (4\text{H}, \text{ m}), 7.16–7.14 \ (3\text{H}, \text{ m}), 7.13–7.09 \ (2\text{H}, \text{ m}), 3.76 \ (1\text{H}, \text{ dd}, \ J = 6.9 \text{ Hz}, 4.3 \text{ Hz}), 3.06 \ (1\text{H}, \text{ dd}, \ J = 14.0 \text{ Hz}, 4.3 \text{ Hz}), 2.95 \ (1\text{H}, \text{ dd}, \ J = 14.0 \text{ Hz}, 6.9 \text{ Hz}), 2.64 \ (3\text{H}, \text{ s}), 1.44 \ (3\text{H}, \text{ s}); ^13\text{C} \text{NMR} \ (125 \text{ MHz, CDCl}_3) \ \delta_C \ 173.5, 141.4, 137.3, 134.1, 129.7, 129.0, 128.6, 126.8, 126.7, 78.2, 59.2, 38.0, 26.2, 21.0; \ \text{LRMS} \ m/z \ (\text{ES}) \ (\text{M+H})^+ = 315.1; \ \text{HRMS} \ m/z \ (\text{ES}) \ (\text{M+H})^+ = 315.1253; \ \text{HRMS} \ m/z \ \text{calc.} \ (\text{M+H})^+ = 315.1264.
(2R,5S)-5-Benzyl-2,3-dimethyl-2-(4-cyanophenyl)imidazolidin-4-one 23

Prepared according to General Procedure. \([\alpha]_D^{20} 41.8 (c 0.1, \text{CH}_3\text{OH}); \nu_{\text{max}} (\text{NaCl disk})/\text{cm}^{-1} 2228, 1695; ^1\text{H} \text{NMR} (500 \text{ MHz, CDCl}_3) \delta_{\text{H}} 7.57 (2\text{H, dt, } J = 10.4 \text{ Hz, } 1.7 \text{ Hz}), 7.31 (2\text{H, dt, } J = 10.4 \text{ Hz, } 1.7 \text{ Hz}), 7.24 (2\text{H, t, } J = 7.5 \text{ Hz}), 7.20–7.15 (3\text{H, m}), 3.72 (1\text{H, dd, } J = 6.3 \text{ Hz, } 4.7 \text{ Hz}), 3.07 (1\text{H, dd, } J = 14.1 \text{ Hz, } 4.7 \text{ Hz}), 3.00 (1\text{H, dd, } J = 14.1 \text{ Hz, } 6.3 \text{ Hz}), 2.99 (3\text{H, s}), 1.94 (1\text{H, s}), 1.45 (3\text{H, s}); ^1\text{C} \text{NMR} (125 \text{ MHz, CDCl}_3) \delta_{\text{C}} 173.6, 147.9, 136.8, 132.7, 129.6, 128.7, 127.0, 126.1, 118.3, 112.1, 78.2, 59.0, 37.6, 26.3, 25.8; \text{LRMS} \ m/z (\text{APCI}) (\text{M}+\text{H}^+) = 306.2; \text{HRMS} \ m/z (\text{ES}) (\text{M}+\text{H}^+) = 306.1600; \text{HRMS} \ m/z \text{ calc.} (\text{M}+\text{H}^+) = 306.1606.

(2R,5S)-5-Benzyl-2,3-dimethyl-2-(4-nitrophenyl)imidazolidin-4-one 24

L-Phenylalanine-N-methyl amide (3.86 g, 21.7 mmol) was dissolved in DMF (20 mL). 4-Nitroacetophenone (3.96 g, 24 mmol) was added followed by methanesulfonic acid (0.3 mL, 4.63 mmol, 20 mol%). The mixture was separated into two microwave vials and subjected to microwave irradiation at 150 °C for 30 minutes. The contents of the two vials were combined and concentrated under reduced pressure. Chloroform (40 mL) and saturated sodium carbonate solution (40 mL) were added. The aqueous layer was extracted with chloroform (2 × 40 mL) and dried over anhydrous potassium carbonate. The solvent was removed under reduced pressure and the residue purified by flash chromatography (20% ethyl acetate in petroleum ether) to give the title compound as an orange oil (500 mg, 7%). \([\alpha]_D^{20} = +24.2 (c=2.0, \text{MeOH}); \nu_{\text{max}} (\text{ATR})/\text{cm}^{-1} 3350, 3028, 2924, 2855, 1688; ^1\text{H} \text{NMR} (400 \text{ MHz, CDCl}_3) \delta 8.26–8.16 (2\text{H, m}), 7.51–7.44 (2\text{H, m}), 7.36–7.22 (5\text{H, m}), 3.83 (1\text{H, app. t, } J = 5.3 \text{ Hz}), 3.18 (1\text{H, dd, } J = 14.1, 4.6 \text{ Hz}), 3.11 (1\text{H, dd, } J = 14.1, 6.5 \text{ Hz}), 2.80 (3\text{H, s}), 2.04 (1\text{H, s}), 1.57 (3\text{H, s}); ^1\text{C} \text{NMR} (101 \text{ MHz, CDCl}_3) \delta 173.7, 150.0, 147.8, 136.9, 129.8, 128.8, 127.1, 126.5, 124.2, 78.2, 59.1, 37.7, 26.4, 26.1; \text{m/z (ES/APCI):} 326.2 (\text{M}+\text{H}^+).
**General Procedure for imidazolidinone salt formation**

A solution of the amine in diethyl ether was treated with hydrogen chloride gas for 10 minutes. The precipitate was recovered on a sinter, washed with diethyl ether and petroleum ether, then dried under reduced pressure.

(S)-5-Benzyl-2,2,3-trimethylimidazolidin-4-one hydrochloride 13·HCl

![Chemical structure](image)

mp: 104–106 °C; $[\alpha]_{D}^{20} = -71.5$ (c=1.3, MeOH); $\nu_{\text{max}}$ (ATR)/cm$^{-1}$ 3416, 3380, 1710; $^1$H NMR (400 MHz, MeOD) $\delta$ 7.49–7.27 (5H, m), 4.67 (1H, dd, $J = 10.7$, 3.5 Hz), 3.53 (1H, dd, $J = 15.2$, 3.5 Hz), 3.09 (1H, dd, $J = 15.2$, 10.7 Hz), 2.92 (3H, s), 1.75 (3H, s), 1.60 (3H, s); $^{13}$C NMR (101 MHz, MeOD) $\delta$ 170.4, 139.2, 132.9, 132.7, 131.3, 81.7, 62.3, 37.5, 28.3, 26.9, 24.9; $m/z$ (ES): 219.0 (M·Cl).

(2R,5S)-5-Benzyl-2-(4-methoxyphenyl)-2,3-dimethylimidazolidin-4-one hydrochloride 20·HCl

![Chemical structure](image)

mp 117–119 °C; $[\alpha]_{D}^{30}$ 36.0 (c 0.1, CH$_3$OH); $\nu_{\text{max}}$ (NaCl disk)/cm$^{-1}$ 3418, 1715, 1608; $^{13}$C NMR (125 MHz, CD$_3$OD) $\delta_{C}$ 165.8, 160.1, 133.4, 127.3, 127.1, 126.3, 125.8, 123.6, 113.1, 78.5, 55.4, 53.1, 32.4, 23.9, 20.1; LRMS $m/z$ (ES) = 311.2 (M–Cl); HRMS $m/z$ (ES) (M–Cl$^-$) = 311.1753; HRMS $m/z$ calc. (M–Cl$^-$) = 311.1760.
(2R,5S)-5-Benzyl-2,3-dimethyl-2-phenylimidazolidin-4-one hydrochloride 21·HCl

mp 139–141 °C; [α]$_D^{10}$ 7.6 (c 0.1, CH$_2$Cl$_2$); $\nu_{\text{max}}$ (NaCl disk)/cm$^{-1}$ 3412, 2096, 1644; $^1$H NMR (500 MHz, CD$_3$OD) δ$_H$ 7.60–7.55 (3H, m), 7.50–7.46 (2H, m), 7.41 (2H, d, $J = 7.6$ Hz), 7.36 (2H, t, $J = 7.6$ Hz), 7.30 (1H, tt, $J = 7.60$ Hz, 2.4 Hz), 4.44 (1H, dd, $J = 9.7$ Hz, 4.0 Hz), 3.57 (1H, dd, $J = 15.2$ Hz, 4.0 Hz), 3.24 (1H, dd, $J = 15.2$ Hz, 9.7 Hz), 2.94 (3H, s), 2.21 (3H, s); $^{13}$C NMR (125 MHz, CD$_3$OD) δ$_C$ 167.6, 134.9, 134.3, 130.8, 129.5, 129.0, 128.8, 127.4, 126.9, 80.5, 58.6, 34.0, 26.2, 19.4; LRMS $m/z$ (ES) = 281.2 (M–Cl$^-$); HRMS $m/z$ (ES) (M–Cl$^-$) = 281.1646; HRMS $m/z$ calc. (M–Cl$^-$) = 281.1654.

(2R,5S)-5-Benzyl-2-(4-chlorophenyl)-2,3-dimethylimidazolidin-4-one hydrochloride 22·HCl

mp 133–135 °C; [α]$_D^{30}$ 38.0 (c 0.1, CH$_3$OH); $\nu_{\text{max}}$ (NaCl disk)/cm$^{-1}$ 3414, 1720, 1495; $^1$H NMR (500 MHz, CD$_3$OD) δ$_H$ 7.58 (2H, dt, $J = 8.8$ Hz, 1.9 Hz), 7.47 (2H, dt, $J = 8.8$ Hz, 1.9 Hz), 7.42 (2H, d, $J = 7.4$ Hz), 7.36 (2H, t, $J = 7.4$ Hz), 7.30 (1H, t, $J = 7.4$ Hz), 4.46 (1H, dd, $J = 9.7$ Hz, 4.0 Hz), 3.57 (1H, dd, $J = 15.2$ Hz, 4.0 Hz), 3.25 (1H, dd, $J = 15.24$ Hz, 9.7 Hz), 2.93 (3H, s), 2.20 (3H, s); $^{13}$C NMR (125 MHz, CD$_3$OD) δ$_C$ 167.3, 136.8, 134.9, 132.4, 129.6, 129.0, 128.7, 128.2, 127.3, 79.6, 58.0, 33.8, 25.5, 22.2; LRMS $m/z$ (APCI) = 315.1 (M–Cl$^-$); HRMS $m/z$ (ES) (M–Cl$^-$) = 315.1257; HRMS $m/z$ calc. (M–Cl$^-$) = 315.1264.
(2R,5S)-5-Benzyl-2,3-dimethyl-2-(4-cyanophenyl)imidazolidin-4-one hydrochloride 23·HCl

mp 109–111 °C; [α]_{D}^{26} +43.6 (c 0.1, CH_{3}OH); \nu_{\text{max}} (NaCl disk)/cm^{-1} 3415, 2534, 2231, 1722; ^1H NMR (500 MHz, CD_{3}OD) δ_{H} 7.91 (2H, d, J = 8.6 Hz), 7.65 (2H, d, J = 8.6 Hz), 7.40 (2H, d, J = 7.5 Hz), 7.34 (2H, t, J = 7.5 Hz), 7.28 (1H, t, J = 7.5 Hz), 6.44 (1H, dd, J = 9.6 Hz, 3.9 Hz), 3.55 (1H, dd, J = 15.2 Hz, 3.9 Hz), 3.23 (1H, dd, J = 15.2 Hz, 9.6 Hz), 2.93 (3H, s), 2.21 (3H, s); ^{13}C NMR (125 MHz, CD_{3}OD) δ_{C} 167.4, 138.7, 134.9, 133.2, 129.0, 128.7, 127.7, 127.3, 117.3, 114.5, 79.3, 58.1, 33.8, 25.6, 22.1; LRMS \text{m/z} (APCI) = 306.1 (M–Cl); HRMS \text{m/z} (ES) (M–Cl) = 306.1597; HRMS \text{m/z} cal. (M–Cl) = 306.1606;

(2R,5S)-5-Benzyl-2,3-dimethyl-2-(4-nitrophenyl)imidazolidin-4-one hydrochloride 24·HCl

mp 153–155 °C; [α]_{D}^{20} = +36.4 (c=2.0, MeOH); \nu_{\text{max}} (ATR)/cm^{-1} 1732; ^1H NMR (400 MHz, CDCl_{3}) δ 8.26 (2H, d, J = 8.8 Hz), 7.58 (2H, d, J = 8.8 Hz), 7.44–7.27 (5H, m), 4.28 (1H, app. t, J = 5.7 Hz), 3.43 (1H, dd, J = 15.1, 5.7 Hz), 3.31 (1H, dd, J = 15.1, 5.7 Hz), 2.80 (3H, s), 1.82 (3H, s); ^{13}C NMR (101 MHz, CDCl_{3}) δ_{C} 167.5, 149.3, 140.9, 134.3, 130.1, 129.1, 128.3, 128.1, 124.6, 79.3, 58.0, 34.6, 26.6, 23.3; \text{m/z} (ES/APCI): 326.1 (M–Cl). HRMS (ES) calculated for C_{18}H_{20}O_{3}N_{3} 326.1499 (M+H+), found 326.1498.

General Procedure for Diels Alder cycloaddition (Tables 2 and 3)

Imidazolidinone hydrochloride salt (0.1 mmol, 5 mol%) was dissolved in a 19:1 methanol/water mixture (2 mL). The flask was placed into a 25 °C oil bath. The appropriate aldehyde (2.0 mmol) was added and the mixture was stirred for 10 minutes before freshly distilled cyclopentadiene (420 \mu L, 5.0 mmol) was added in one portion. The reaction mixture was stirred for 6 h and then the volatiles were removed under reduced pressure. The residue was taken up into chloroform (10 mL) and water (10
mL) and the aqueous layer was extracted with chloroform (2 × 10 mL). The combined organics were dried over sodium sulfate and the solvent was removed under reduced pressure. Chloroform (2 mL), water (1 mL) and TFA (1 mL) were added and the biphasic mixture was vigorously stirred for 2 hours. Potassium carbonate (20 mL) was added and the mixture was extracted with chloroform (3 × 10 mL). The combined organics were dried over sodium sulfate and the solvent was removed under reduced pressure. The products were isolated using flash chromatography (10% ethyl acetate in petroleum ether) as oils.

Monitoring Diels-Alder cycloaddition between cinnamaldehyde and cyclopentadiene (Figure 5)

Secondary amine salt (0.25 mmol, 5 mol%) was dissolved in methanol (4.75 mL) and water (0.25 mL). The mixture was stirred at 25 °C. After 5 minutes, cinnamaldehyde (630 µL, 5 mmol) was added. After another 10 minutes, freshly distilled cyclopentadiene (1020 µL, 12.5 mmol) was added and the reaction timer started. 100 µL aliquots were periodically removed and concentrated under reduced pressure (25 °C, 15 torr, 10 minutes). Water (5 mL) was added and extracted with diethyl ether (3 × 5 mL). The combined organics were concentrated under reduced pressure. Chloroform (2 mL) was added followed by a mixture of TFA/water 1:1 (2 mL). The biphasic mixture was vigorously stirred for 2 h. The reaction was quenched with saturated sodium carbonate solution (5 mL) and extracted with diethyl ether (3 × 5 mL). The combined organics were dried over magnesium sulfate and the solvent was removed under reduced pressure to give a yellow oil. 1H NMR (CDCl3) was used to assess reaction conversion from the CHO resonances: exo 9.93 ppm (1H, d, J = 2.0 Hz, CHO), cinnamaldehyde 9.71 ppm (1H, d, J = 7.7 Hz, CHO) and endo 9.60 ppm (1H, d, J = 2.2 Hz, CHO). The Diels-Alder adducts can be isolated by flash chromatography (20% ethyl acetate in petroleum ether) to give a pale yellow viscous oil.

endo-3-Phenylbicyclo[2.2.1]hept-5-ene-2-carbaldehyde 26 and exo-3-Phenylbicyclo[2.2.1]hept-5-ene-2-carbaldehyde 27

endo/exo mixture

endo/exo mixture νmax (film)/cm⁻¹ 3414, 2972, 1717; exo 1H NMR (500 MHz, CDCl3) δ 9.93 (1H, d, J = 2.0 Hz), 7.41–7.12 (5H, m), 6.35 (1H, dd, J = 5.5, 3.5 Hz), 6.09 (1H, dd, J = 5.5, 2.9 Hz), 3.77–3.72 (1H, m), 3.26–3.21 (2H, m), 2.62–2.58 (1H, m), 1.66–1.55 (2H, m); endo 1H NMR (500 MHz, CDCl3) δ 9.61 (1H, d, J = 2.2 Hz), 7.38–7.11 (5H, m), 6.43 (1H, dd, J = 5.6, 3.2 Hz), 6.19 (1H, dd, J = 5.6, 2.8 Hz), 3.35 (1H, br. s), 3.16–3.09 (1H, m), 3.03–2.96 (1H, m), 1.60–1.55 (2H, m); endo/exo
mixture $^{13}$C NMR (126 MHz, CDCl$_3$) δ 203.4, 202.8, 143.6, 142.7, 139.3, 136.6, 136.4, 133.9, 128.7, 128.2, 127.9, 127.4, 126.4, 126.3, 60.9, 59.5, 48.5, 48.4, 47.6, 47.2, 45.8, 45.5, 45.5, 45.2; m/z (EI): 198.1 (M$^+$).

*endo*-3-(4-Methoxyphenyl)bicyclo[2.2.1]hept-5-ene-2-carbaldehyde and *exo*-3-(4-methoxyphenyl)bicyclo[2.2.1]hept-5-ene-2-carbaldehyde Table 3 Entry 1

![Diagram of endo-exo mixture](image)

endo/exo mixture $\nu_{\text{max}}$ (film)/cm$^{-1}$: 2965, 2934, 2907, 2833, 1712; *exo* $^1$H NMR (500 MHz, CDCl$_3$) δ 9.92 (1H, d, $J = 2.1$ Hz, CHO), 7.10–7.06 (2H, m), 6.83–6.79 (2H, m), 6.35 (1H, dd, $J = 5.6$, 3.2 Hz), 6.08 (1H, dd, $J = 5.6$, 2.9 Hz), 3.78 (3H, s), 3.67 (1H, dd, $J = 5.1$, 3.7 Hz), 3.22 (1H, s), 3.18 (1H, s), 2.56–2.53 (1H, m), 1.64–1.60 (1H, m), 1.58–1.54 (1H, m); *endo* $^1$H NMR (500 MHz, CDCl$_3$) δ 9.59 (1H, d, $J = 2.3$ Hz, CHO), 7.22–7.18 (2H, m), 6.88–6.84 (2H, m), 6.42 (1H, dd, $J = 5.6$, 3.2 Hz), 6.17 (1H, dd, $J = 5.6$, 2.8 Hz), 3.80 (3H, s), 3.33 (1H, s), 3.08 (1H, s), 3.04 (1H, d, $J = 4.5$ Hz), 2.96–2.93 (1H, m), 1.80 (1H, app. d, $J = 8.7$ Hz), 1.64–1.60 (1H, m); endolexoxo mixture $^{13}$C NMR (126 MHz, CDCl$_3$) δ 203.8, 203.0, 158.3, 158.1, 139.4, 136.7, 136.4, 135.7, 134.8, 133.8, 128.9, 128.4, 114.1, 113.7, 61.0, 59.8, 55.4, 55.4, 48.8, 48.7, 47.7, 47.2, 45.6, 45.2, 45.2, 44.9; due to fragmentation, mass spectrometric analysis of the parent aldehydes was not possible; m/z of corresponding alcohols (CI): 231.1 (M+H$^+$).

*endo*-3-(4-Methylphenyl)bicyclo[2.2.1]hept-5-ene-2-carbaldehyde and *exo*-3-(4-methylphenyl)bicyclo[2.2.1]hept-5-ene-2-carbaldehyde Table 3 Entry 2

![Diagram of endo-exo mixture](image)

endo/exo mixture $\nu_{\text{max}}$ (film)/cm$^{-1}$: 2968, 2941, 2918, 2874, 2912, 2710, 1715; *exo*: $^1$H NMR (500 MHz, CDCl$_3$) δ 9.92 (1H, d, $J = 2.1$ Hz, CHO), 7.09–7.03 (4H, m), 6.34 (1H, dd, $J = 5.7$, 3.2 Hz), 6.08 (1H, dd, $J = 5.7$, 2.9 Hz), 3.69 (1H, dd, $J = 5.2$, 3.2 Hz), 3.24–3.19 (2H, m), 2.57 (1H, app. dt, $J = 5.2$, 1.8 Hz), 2.31 (3H, s), 1.64–1.53 (2H, m); *endo*: $^1$H NMR (500 MHz, CDCl$_3$) δ 9.60 (1H, d, $J =$
2.3 Hz), 7.20–7.11 (4H, m), 6.42 (1H, dd, J = 5.6, 3.2 Hz), 6.17 (1H, dd, J = 5.6, 2.8 Hz), 3.33 (1H, s), 3.10 (1H, s), 3.05 (1H, d, J = 4.6 Hz), 2.98–2.95 (1H, m), 2.33 (3H, s), 1.81 (1H, app. d, J = 8.7 Hz), 1.64–1.53 (1H, m); endo/exo mixture: $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 203.7, 203.0, 140.6, 139.7, 139.3, 136.7, 136.4, 136.0, 135.9, 133.9, 129.4, 129.0, 127.9, 127.4, 60.9, 59.6, 48.7, 48.5, 47.7, 47.2, 45.6, 45.5, 45.2, 21.0; due to fragmentation, mass spectrometric analysis of the parent aldehydes was not possible; m/z of corresponding alcohol (Cl): 215.1 (M+H$^+$).

**endo-3-(4-Chlorophenyl)bicyclo[2.2.1]hept-5-ene-2-carbaldehyde and exo-3-(4-chlorophenyl)bicyclo[2.2.1]hept-5-ene-2-carbaldehyde**

*Table 3 Entry 3*

endo/exo mixture $\nu_{\text{max}}$ (film)/cm$^{-1}$: 3061, 2970, 2872, 2810, 2712, 1715; **exo**: $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 9.91 (1H, d, J = 1.8 Hz, CHO), 7.24–7.20 (2H, m), 7.10–7.06 (2H, m), 6.36 (1H, dd, J = 5.6, 3.2 Hz), 6.06 (1H, dd, J = 5.6, 2.9 Hz), 3.71 (1H, dd, J = 5.1, 3.6 Hz), 3.26–3.22 (1H, m), 3.19 (1H, br. s), 2.52–2.55 (1H, m), 1.62–1.56 (2H, m); **endo**: $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 9.60 (1H, d, J = 2.1 Hz), 7.30–7.26 (2H, m), 7.22–7.19 (2H, m), 6.42 (1H, dd, J = 5.7, 3.2 Hz), 6.18 (1H, dd, J = 5.7, 2.8 Hz), 3.36 (1H, s), 3.12–3.08 (1H, m), 3.07 (1H, d, J = 4.1 Hz), 2.95–2.90 (1H, m), 1.77 (1H, app. d, J = 8.7 Hz), 1.67–1.63 (1H, m); endo/exo mixture: $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 203.1, 202.4, 142.2, 141.2, 139.3, 136.6, 136.4, 133.9, 132.2, 132.1, 129.3, 128.8, 128.3, 61.1, 59.7, 48.5, 48.4, 47.7, 47.2, 45.6, 45.2, 45.2, 44.9; m/z (EI): 232.0 (M$^+$); HRMS (EI) calculated for C$_{14}$H$_{13}$OCl$^{35}$ 232.0649 (M$^+$), found 232.0652.
Table 3 Entry 4

**endo/exo mixture** $v_{\text{max}}$ (film)/cm$^{-1}$: 3063, 2972, 2943, 2872, 2818, 2717, 1713, 1713, 1514, 1342; **exo**: $^1$H NMR (500 MHz, CDCl$_3$) δ 9.90 (1H, d, $J = 1.4$ Hz, CHO), 8.07 (2H, d, $J = 8.7$ Hz), 7.28 (2H, d, $J = 8.7$ Hz), 6.39 (1H, dd, $J = 5.6$, 3.2 Hz), 6.03 (1H, dd, $J = 5.6$, 2.8 Hz), 3.88–3.84 (1H, m), 3.28 (1H, s), 3.24 (1H, s), 2.61 (1H, app. d, $J = 5.1$ Hz), 1.59 (2H, br. s); **endo**: $^1$H NMR (500 MHz, CDCl$_3$) δ 9.62 (1H, d, $J = 1.4$ Hz, CHO), 8.13 (2H, d, $J = 8.6$ Hz), 7.41 (2H, d, $J = 8.6$ Hz), 6.42 (1H, dd, $J = 3.3$ Hz), 6.18 (1H, dd, $J = 5.6$, 3.0 Hz), 3.41 (1H, s), 3.19 (1H, d, $J = 4.9$ Hz), 3.17 (1H, s), 2.96–2.93 (1H, m), 1.77–1.66 (2H, m); **endo/exo mixture**: $^{13}$C NMR (126 MHz, CDCl$_3$) δ 202.2, 201.6, 151.7, 150.7, 146.6, 146.5, 139.1, 137.1, 136.1, 134.1, 128.8, 128.3, 123.9, 123.4, 61.2, 59.6, 48.5, 48.0, 47.7, 47.2, 45.7, 45.6, 45.2, 45.1; due to fragmentation, mass spectrometric analysis of the parent aldehydes was not possible; m/z of corresponding alcohol (Cl): 246.1 (M+H$^+$).

Table 3 Entry 5

**endo-3-Propylbicyclo[2.2.1]hept-5-ene-2-carbaldehyde and exo-3-propylbicyclo[2.2.1]hept-5-ene-2-carbaldehyde**

Secondary amine salt (0.1 mmol, 1 mol%) was dissolved in methanol (9.5 mL) and water (0.5 mL). The mixture was stirred at 25 °C. *trans*-2-Hexenal (1.16 mL, 10 mmol) was added and the mixture stirred for 10 minutes before freshly distilled cyclopentadiene (2.00 mL, 25 mmol) was added. After 18 h the solvent was removed under reduced pressure (100 mbar, 25 °C). Water (20 mL) and diethyl ether (20 mL) were added to the residue and the aqueous layer extracted with diethyl ether (2 × 20 mL). The organics were dried over sodium sulfate and the solvent removed under reduced pressure (100 mbar, 25 °C). Chloroform (4 mL) was added to the residue followed by a 1:1 water and TFA mixture (4 mL). The biphase was vigorously stirred for 2 hours. The reaction was then quenched with saturated sodium carbonate solution and the aqueous layer extracted with diethyl ether (3 × 20 mL). The combined organics were dried over sodium sulfate and the solvent removed under reduced pressure (100 mbar, 25 °C). The product was isolated by flash chromatography (5% diethyl ether in...
petroleum ether) to give a colourless oil. $\nu_{\text{max}}$ (ATR)/cm$^{-1}$: 2957, 2918, 2870, 1717; $exo$ $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.77 (1H, d, $J = 2.7$ Hz, CHO, 6.20 (1H, dd, $J = 5.6, 3.1$ Hz), 6.13 (1H, dd, $J = 5.6, 2.9$ Hz), 3.01 (1H, s, $J = 1.3$ Hz), 2.87 (1H, s), 2.32–2.24 (1H, m), 1.77–1.73 (1H, m), 1.55–1.04 (6H, m), 0.90 (3H, t, $J = 7.1$ Hz); $endo$ $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.36 (1H, d, $J = 3.4$ Hz), 6.27 (1H, dd, $J = 5.7, 3.2$ Hz), 6.05 (1H, dd, $J = 5.7, 2.9$ Hz), 3.11 (1H, s), 2.66 (1H, d, $J = 1.5$ Hz), 2.37 (1H, dd, $J = 7.8, 3.4$ Hz), 1.71–1.65 (1H, m), 1.56–1.03 (6H, m), 0.90 (3H, t, $J = 7.1$ Hz).

endo-$3$-isopropylbicyclo[$2.2.1$]hept-$5$-ene-$2$-carbaldehyde and $exo$-$3$-isopropylbicyclo[$2.2.1$]hept-$5$-ene-$2$-carbaldehyde Table 3 Entry 6

Secondary amine salt (0.1 mmol, 1 mol%) was dissolved in methanol (9.5 mL) and water (0.5 mL). The mixture was stirred at 25 $^\circ$C. trans-$4$-Methyl-$2$-hexenal (1.16 mL, 10 mmol) was added and the mixture stirred for 10 minutes before freshly distilled cyclopentadiene (2.00 mL, 25 mmol) was added. After 18 h the solvent was removed under reduced pressure (100 mbar, 25 $^\circ$C). Water (20 mL) and diethyl ether (20 mL) were added to the residue and the aqueous layer extracted with diethyl ether ($2 \times 20$ mL). The organics were dried over sodium sulfate and the solvent removed under reduced pressure (100 mbar, 25 $^\circ$C). Chloroform (4 mL) was added to the residue followed by a 1:1 water and TFA mixture (4 mL). The biphasic was vigorously stirred for 2 hours. The reaction was then quenched with saturated sodium carbonate solution and the aqueous layer extracted with diethyl ether (3 $\times$ 20 mL). The combined organics were dried over sodium sulfate and the solvent removed under reduced pressure (100 mbar, 25 $^\circ$C). The product was isolated by flash chromatography (5% diethyl ether in petroleum ether) to give a colourless oil. $\nu_{\text{max}}$ (ATR)/cm$^{-1}$: 2957, 2911, 2895, 2870, 1701; $exo$ $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.75 (1H, d, $J = 2.6$ Hz, CHO) 6.26 (1H, dd, $J = 5.3, 3.3$ Hz), 6.07 (1H, dd, $J = 5.7, 2.8$ Hz), 3.11 (1H, s, CH$_2$), 2.87–2.3 (1H, m), 2.51–2.47 (1H, m), 1.51–1.39 (1H, m), 1.34–1.29 (1H, m), 1.01 (1H, d, $J = 6.5$ Hz), 0.91 (1H, d, $J = 6.6$ Hz); $endo/exo$ mixture $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 205.4, 204.3, 139.1, 136.4, 135.9, 133.2, 58.8, 58.1, 50.4, 50.2, 47.0, 46.6, 45.3, 45.3, 45.1, 45.1, 32.9, 32.6, 22.1, 22.1, 21.9, 21.6; $m/z$ (CI): 181 (M$^+$CH$_3$), 163 (M-H).
General procedure for monitoring reaction between cinnamaldehyde and N-methyl pyrrole

\((S)-3-(1\text{-Methyl-1H-pyrrol-2-yl})-3\text{-phenylpropan-1-ol}\)

Secondary amine salt (10 mol%, 0.21 mmol) was dissolved in THF (4 mL) and water (0.6 mL). The mixture was stirred at 25 °C and after 5 minutes cinnamaldehyde (250 µL, 2 mmol) was added. Stirring was continued for 10 minutes before N-methyl pyrrole (530 µL, 5.97 mmol) was added in one portion. Aliquots (100 µL) were periodically taken and added to a mixture of sodium borohydride (5 mg, 0.13 mmol) in ethanol (1 mL). After 15 minutes the reduction was quenched with saturated sodium bicarbonate solution (5 mL) and extracted with dichloromethane (2 × 10 mL). The organics were dried over sodium sulfate and the solvent removed under reduced pressure. The residue was analysed by \(^1\)H NMR to determine reaction conversion using resonances: 4.33 ppm (2H, dd, CH\(_2\)OH) from cinnamyl alcohol and 4.15 (1H, t, PhCH) from the product. The product was isolated using flash chromatography (16% ethyl acetate in petroleum ether) as a colourless oil. \(\nu_{\text{max}}\) (ATR)/cm\(^{-1}\) 3246, 2965, 2930, 2864; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.34–7.28 (2H, m, CH), 7.24–7.17 (3H, m, CH), 6.58–6.54 (1H, m, CH), 6.20–6.14 (2H, m, CH), 4.15 (1H, app. t, \(J = 7.6\) Hz, PhCH), 3.74–3.57 (2H, m, CH\(_2\)OH), 3.32 (3H, s, NCH\(_3\)), 2.42–2.31 (1H, m, CHH), 2.17–2.07 (1H, m, CHH), 1.78 (1H, s, OH); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 143.6, 135.0, 128.6, 128.0, 126.4, 121.9, 106.4, 105.8, 60.6, 39.5, 39.0, 33.9; \(m/z\) (ES): 216.0 (M+H\(^+\)).
**Determination of enantiomeric excesses**

To determine the enantiomeric excess of the Diels-Alder adducts they were derivatised and then analysed by HPLC on a chiral stationary phase. The aldehydes were transformed into their corresponding 2,4-dinitrophenylhydrazones or alcohols using the procedures below:

**General Method for Hydrazone Formation**

2,4-Dinitrophenylhydrazine (100 mg, 0.5 mmol, 2 eq.) was added to aldehyde (0.25 mmol, 1 eq.). A mixture of ethanol (2 mL) and 2.4 M hydrochloric acid (0.2 mL) was then added. The orange suspension was then vigorously stirred until all aldehyde had been consumed by TLC (~4–10 h). The solvent was removed under reduced pressure and the residue was subjected to flash chromatography (20% ethyl acetate in petroleum ether) and the hydrazones were obtained as yellow/orange solids. It should be noted that, due to streaking, chromatography of these species was not quantitative. In addition, diastereomeric ratios were observed to change from the chromatographic process; hence, diastereomeric ratios were determined from the aldehyde precursors.

**General Method for Reduction of Aldehydes with NaBH₄ for HPLC**

Aldehyde (0.24 mmol, 1 eq.) was dissolved in ethanol (1 mL). Sodium borohydride (10 mg, 0.26 mmol, 1.1 eq.) was added. The mixture was stirred until complete consumption of the aldehyde was observed by TLC (~1 h). The flask contents were then poured into a separatory funnel containing saturated ammonium chloride (5 mL) and water (5 mL). The organics were extracted into chloroform (3 × 5 mL) and dried over sodium sulfate. The solvent was removed under reduced pressure. The residue was subjected to flash chromatography (25% ethyl acetate in petroleum ether) and the alcohols were obtained as colourless oils.
Conditions and retention times for compounds analysed by HPLC on a chiral stationary phase

2,4-DNP = Dinitrophenylhydrazone of the corresponding aldehyde

<table>
<thead>
<tr>
<th>Compound</th>
<th>Derivatised to</th>
<th>HPLC Conditions</th>
<th>Retention Times (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="image" /></td>
<td>N/A</td>
<td>Chiralpak IC, 30 °C, 1 mL min⁻¹, 10% IPA in Hexanes</td>
<td>( t_r(S) = 21.8 ) ( t_r(R) = 27.4 )</td>
</tr>
<tr>
<td><img src="image2.png" alt="image" /></td>
<td>N/A</td>
<td>Chiralcel OJ, 25 °C, 1.5 mL min⁻¹, 10% IPA in Hexanes</td>
<td>( t_r(2S,5R) = 40.0 ) ( t_r(2R,5S) = 47.9 )</td>
</tr>
<tr>
<td><img src="image3.png" alt="image" /></td>
<td>2,4-DNP</td>
<td>Chiralcel OD-R, 25 °C, 0.85 mL min⁻¹, 75% MeCN in H₂O</td>
<td>( t_r(1R,2S,3S,4S) = 22.8 ) ( t_r(1S,2R,3R,4R) = 28.9 )</td>
</tr>
<tr>
<td><img src="image4.png" alt="image" /></td>
<td>2,4-DNP</td>
<td>Chiralcel OD-R, 25 °C, 0.85 mL min⁻¹, 75% MeCN in H₂O</td>
<td>( t_r(1S,2S,3S,4R) = 32.6 ) ( t_r(1R,2R,3R,4S) = 44.1 )</td>
</tr>
<tr>
<td><img src="image5.png" alt="image" /></td>
<td>2,4-DNP</td>
<td>Chiralpak IB, 20 °C, 1 mL min⁻¹, 10% IPA in Hexanes</td>
<td>( t_r(1R,2S,3S,4S) = 9.7 ) ( t_r(1S,2R,3R,4R) = 10.5 )</td>
</tr>
<tr>
<td><img src="image6.png" alt="image" /></td>
<td>2,4-DNP</td>
<td>Chiralpak IA, 20 °C, 0.5 mL min⁻¹, 2.5% IPA in Hexanes</td>
<td>( t_r(1R,2R,3R,4S) = 32.2 ) ( t_r(1S,2S,3S,4R) = 35.9 )</td>
</tr>
<tr>
<td><img src="image7.png" alt="image" /></td>
<td>2,4-DNP</td>
<td>Chiralpak IB, 20 °C, 0.75 mL min⁻¹, 10% IPA in Hexanes</td>
<td>( t_r(1R,2S,3S,4S) = 13.0 ) ( t_r(1S,2R,3R,4R) = 13.9 )</td>
</tr>
<tr>
<td><img src="image8.png" alt="image" /></td>
<td>2,4-DNP</td>
<td>Chiralpak IB, 20 °C, 0.75 mL min⁻¹, 10% IPA in Hexanes</td>
<td>( t_r(1R,2R,3R,4S) = 18.3 ) ( t_r(1S,2S,3S,4R) = 19.4 )</td>
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<tr>
<td><img src="image9.png" alt="image" /></td>
<td>Alcohol</td>
<td>Chiralpak IC, 20 °C, 1 mL min⁻¹, 5% IPA in Hexanes</td>
<td>( t_r(1S,2R,3R,4R) = 10.2 ) ( t_r(1R,2S,3S,4S) = 8.2 )</td>
</tr>
<tr>
<td>Compound</td>
<td>Chiralpak</td>
<td>Temperature</td>
<td>Flow Rate</td>
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<tr>
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</table>
| Alcohol  | IC        | 20 °C       | 1 mL min⁻¹ | 5% IPA in Hexanes | t₁(1R,2R,3R,4S) = 7.6  
|          |           |             |           |              | t₁(1S,2S,3S,4R) = 9.5 |
| Alcohol  | IB        | 20 °C       | 1 mL min⁻¹ | 2.5% IPA in Hexanes | t₁(1S,2R,3R,4R) = 13.3  
|          |           |             |           |              | t₁(1R,2S,3S,4R) = 18.6 |
| Alcohol  | IB        | 20 °C       | 1 mL min⁻¹ | 2.5% IPA in Hexanes | t₁(1R,2R,3R,4S) = 14.2  
|          |           |             |           |              | t₁(1S,2S,3S,4R) = 21.4 |
| Alcohol  | IB        | 20 °C       | 0.75 mL min⁻¹ | 10% IPA in Hexanes | t₁(1S,2R,3R,4R) = 9.6  
|          |           |             |           |              | t₁(1R,2S,3S,4R) = 11.0 |
| Alcohol  | IB        | 20 °C       | 0.75 mL min⁻¹ | 10% IPA in Hexanes | t₁(1R,2R,3R,4S) = 9.2  
|          |           |             |           |              | t₁(1S,2S,3S,4R) = 12.3 |
| Alcohol  | IA        | 27.5 °C     | 0.75 mL min⁻¹ | 10% IPA in Hexanes | t₁(1R,2S,3S,4R) = 48.0  
|          |           |             |           |              | t₁(1R,2S,3R,4R) = 51.2 |
| Alcohol  | IA        | 27.5 °C     | 0.75 mL min⁻¹ | 10% IPA in Hexanes | t₁(1R,2R,3R,4S) = 43.1  
|          |           |             |           |              | t₁(1S,2S,3S,4R) = 45.0 |
General Method for Calculating PA of catalysts

Proton affinity values were calculated using methodology described by Rao and Sastry.\textsuperscript{2} Calculations were performed using the Gaussian03 suite of programmes\textsuperscript{3} using a B3LYP functional and 6-31+G** basis set as previously documented.\textsuperscript{4}
Preparation and Table of X-Ray Data for Isolated Iminium Ion

(2S,5S,E)-5-Benzyl-1-((E)-3-(4-iodophenyl)allylidene)-2,3-dimethyl-2-(4-nitrophenyl)-4-oxoimidazolidin-1-ium hexafluorophosphate

65% Hexafluorophosphoric acid solution (1.00 mL, 7.35 mmol) was added to ethanol (10 mL). Activated 3 Å molecular sieves (1 g) were added and the mixture left overnight to give a ~7.0 M solution of HPF₆ in ethanol (after 3 days the solution degrades and should be disposed of).

(2R,5S)-5-Benzyl-2,3-dimethyl-2-(4-nitrophenyl)imidazolidin-4-one (190 mg, 0.58 mmol) was dissolved in anhydrous ethanol (2 mL). 4-Iodocinnamaldehyde (143 mg, 0.55 mmol) was added followed by 0.7M ethanolic hexafluorophosphoric acid (0.85 mL, 0.59 mmol). The mixture was stirred for 1 h. to give a yellow gum. The supernatant was removed with a syringe. The residue was washed with anhydrous ethanol (2 × 5 mL), diethyl ether (5 mL) and then dried under reduced pressure to give a yellow powder (200 mg, 51%). mp (decomp.): 148–151 °C; ν max (ATR)/cm⁻¹ 3082, 1721, 1614, 1595, 1568, 1524; ¹H NMR (500 MHz, CD₃CN) δ 8.31–8.27 (2H, m), 8.20 (1H, dd, J = 10.8, 1.8 Hz), 7.98 (2H, d, J = 8.5 Hz), 7.87 (1H, d, J = 14.8 Hz), 7.72–7.67 (2H, m), 7.52 (2H, d, J = 8.5 Hz), 7.40–7.27 (3H, m), 7.21–7.12 (3H, m, CH₃), 5.42 (1H, app. t, J = 4.1 Hz), 3.69 (1H, dd, J = 14.8, 5.7 Hz), 3.57 (1H, dd, J = 14.8, 4.2 Hz), 2.56 (3H, s), 1.36 (3H, s); ¹³C NMR (126 MHz, CD₃CN) δ 170.3, 167.2, 165.8, 150.5, 144.0, 140.1, 134.9, 133.7, 131.3, 130.4, 130.2, 129.5, 125.5, 118.7, 104.8, 87.9, 65.3, 37.7, 26.6, 22.6; ¹⁹F NMR (376 MHz, CD₃CN) δ -72.9 (d, J = 706 Hz, PF₆); ³¹P NMR (162 MHz, CD₃CN) δ -144.6 (hept, J = 706 Hz, PF₆); m/z (ES): 566.0 (M-PF₆); HRMS (ES) calculated for C₂₇H₂₅O₃N₃I 566.0935 (M-PF₆), found 566.0930.
Crystal data and structure refinement (CCCD 1017471)

Identification code tomp_jhr592
Empirical formula C29 H30 F6 I N3 O3.50 P
Formula weight 748.43
Temperature 123(2) K
Wavelength 1.54180 Å
Crystal system Triclinic
Space group P-1
Unit cell dimensions
\[ a = 10.4383(4) \text{ Å} \quad \alpha = 86.399(4)^\circ. \]
\[ b = 16.5706(7) \text{ Å} \quad \beta = 86.024(4)^\circ. \]
\[ c = 18.8976(9) \text{ Å} \quad \gamma = 73.657(4)^\circ. \]
Volume 3125.9(2) Å^3
Z 4
Density (calculated) 1.590 Mg/m^3
Absorption coefficient 9.185 mm^{-1}
F(000) 1500
Crystal size 0.40 x 0.18 x 0.06 mm^3
Theta range for data collection 4.42 to 73.56°.
Index ranges -12<=h<=12, -20<=k<=20, -23<=l<=23
Reflections collected 25306
Independent reflections 25307 [R(int) = 0.0000]
Completeness to theta = 70.00° 99.6 %
Absorption correction Analytical
Max. and min. transmission 0.613 and 0.182
Refinement method Full-matrix least-squares on F^2
Data / restraints / parameters 25307 / 0 / 791
Goodness-of-fit on F^2 1.053
Final R indices [I>2sigma(I)]
\[ R1 = 0.0564, \text{ wR}2 = 0.1354 \]
R indices (all data)
\[ R1 = 0.0735, \text{ wR}2 = 0.1501 \]
Largest diff. peak and hole 1.985 and -0.891 e.Å^{-3}
$^1$H and $^{13}$C NMR Spectra and HPLC Chromatograms
$^1$H NMR and e.e. determination traces for Table 3 Entry 1
$^1$H NMR and e.e. determination traces for Table 3 Entry 2
$^1$H NMR and e.e. determination traces for Table 3 Entry 3
$^1$H NMR and e.e. determination traces for Table 3 Entry 4
$^1$H NMR and e.e. determination traces for Table 3 Entry 5
$^1$H NMR and e.e. determination traces for Table 3 Entry 6
$^1$H and $^{13}$C NMR for reduced 32
References